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# BIOGEOCHEMICAL EXPLORATION FOR Mo IN CENTRAL-SOUTH B.C.

by

© RORY DOUGLAS MOIR

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

AND RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS

FOR THE DEGREE OF MASTER OF SCIENCE

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled Biogeochemical Exploration for Mo in Central-South B.C.

submitted by Rory D. Moir

in partial fulfilment of the requirements for the degree of Master of Science

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DATE: 18th September, 1978

## ABSTRACT

The Carmi Mo-(U) deposit is a granodiorite hosted porphyry Mo association located in central South British Columbia in the Omineca Crystalline Belt.

The area has a variety of topographies, from flat plateau to steep-sided gully, at an elevation of 1200 m. A poor mountainous podzol has developed on the till cover which has been populated by Western Larch *Larix occidentalis* , Lodgepole Pine *Pinus contorta* , White Spruce *Picea glauca* and various deciduous bushes and grasses. The trees are young since the area was recently burnt. Western Larch and Lodgepole Pine were sampled since they were the most abundant species.

*"Biogeochemistry"* theory is examined thoroughly from the availability and transport of elements in the substrate to assimilation and mobility within the plant. Variations in plant elemental content and exclusion mechanisms are emphasized and analyzed in relation to this work's findings. The advantages and disadvantages of *"Biogeochemistry"* are examined. Previous work in Mo "Biogeochemistry" both in Canada and the rest of the world is dealt with.

This study's field and laboratory work is extensively detailed. The sampling difficulties including monotony, collection time and the absence of certain species at some localities are considered. Various analytical techniques for U were tried before it was decided that the vegetation contained no U despite the occasional presence of brannerite.

Soil geochemistry is considered in an attempt to explain the "B"

horizon soil elemental variations in relation to measured pH and EL values at selected sample sites. The average pH and Eh is 5.8 and +505 mv respectively.

Analysis of the data showed that exclusion mechanisms were operating on Cu and Zn as well as some other unknown complicating factor which is operating on Pb. Mo did not show any evidence of exclusion mechanisms. Background and threshold values were calculated. Various maps were drawn, the best of which (Western Larch needles, 20 ppm Mo) outlined the known overburden covered limits of the deposit very well. Depth of overburden seemed to have no effect on the success of the method. Other maps are presented which outline the deposit with varying degrees of success.

It was concluded that regional soil sampling for Mo in the "B" soil horizon should be used to define anomolous areas. Western Larch needle *"Biogeochemistry"* should then be used to define the deposit limits.

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# CHAPTER 1

# INTRODUCTION

## Objectives of this Study

This orientation study was undertaken in the hope that a biogeochemical technique could be developed to aid in the discovery of porphyry Mo deposits in central-south British Columbia. Since biogeochemical exploration depends on a wide range of physiological, physiographical and climatic variables, an orientation survey is required for every new area or type of deposit explored. This study examined these variables and how they apply to the Carmi area. The results of this work are intended to be a guide to indicate which organ of a particular species of wide ranging plant would be most suitable for defining areas of anomolously high Mo content.

## Location and Access

The Carmi Mo-(U) deposit is situated in central-south British Columbia at 49° 31' N latitude, 119° 10' W longitude in the Greenwood mining division. The study area is located 3 miles northwest of the small, almost abandoned settlement of Carmi. Kelowna is 50 miles to the north and Beaverdell, the nearest supply source, lies 5 miles to the south of Carmi. There is a discontinued C.P.R. line connecting Carmi with Penticton and Kelowna. A system of logging roads allows access to the study area.

## Reasons for Choosing The Carmi Area

An orientation survey requires that the proposed technique be tried over a known deposit of the type that is to be explored using the intended techniques. Since Carmi has not yet been extensively developed, the area remains largely unaffected by man. This point is essential to the success of a biogeochemical survey since changes to the natural environment can, in many cases, be detected by biogeochemical methods. This point is noted in this work and by Warren and Delavault (1960) who showed that the Pb content of plants growing near a highway were very high and remained anomolous one hundred metres on either side of the road.

Carmi is located in a porphyry Mo province with good prospects of there being other deposits lying undiscovered in the region. Mo is considered to be an "easy" element for use in biogeochemical work (Brooks, 1972). The deposit at Carmi is well documented and its boundaries have been defined by Kenyon (1978). Access to Carmi is very good and Vestor Explorations Ltd. were most cooperative and receptive to sample gathering on their property.

Warren et. al. (1965, 1966a) have done some work on Mo uptake by plants at various producing mines in British Columbia but their work tended to be on relatively few samples and was not carried out on rigorous sampling grids. Also this work was conducted in central British Columbia, far from this study area, where several control factors are dissimilar to those at Carmi. Hornbrook (1969, 1970) has also worked on the biogeochemistry of some central British Columbia Mo deposits. These authors' work is discussed in Chapter 3.

## Geology

This brief description of the area is summarized from Kenyon (1978). Figure 1 shows the regional geology around Carmi.

Carmi lies close to the borders of the Omineca Crystalline and Intermontaine Belts. Pre-Cambrian to Tertiary sedimentary, intrusive and extrusive units are all present in the region. The main rocks in the study area are the Jurassic Nelson batholith and the Cretaceous Valhalla batholith. Permian Anarchist Group roof pendants contain precious metal bearing shear zones which were mined in the 1920's.

The Nelson batholith consists of foliated pink to grey granodiorite with many other acid to intermediate differentiates evident. The Nelson granodiorite and quartz diorite were brecciated and mineralized by the intrusion of the Valhalla, and show propylitic-phyllic- and minor potassic-alteration.

The Valhalla does not outcrop in the area but is shown to underlie the Nelson by drill hole information. The Valhalla consists of foliated white to pink, granite to quartz monzonite and cuts or grades into the Nelson batholith. It is thought that both plutons had a common parent magma since they both have variable textures and similar chemical compositions.

A system of north-south normal faults crosses the region. The mineralized areas also show jointing and fracturing.

Generally breccia constitutes the deposit host rock, however, fractured country rocks can contain significant amounts of Mo (i.e. 0.10% $MoS_2$). The opaque minerals include molybdenite, brannerite, chalcopyrite,

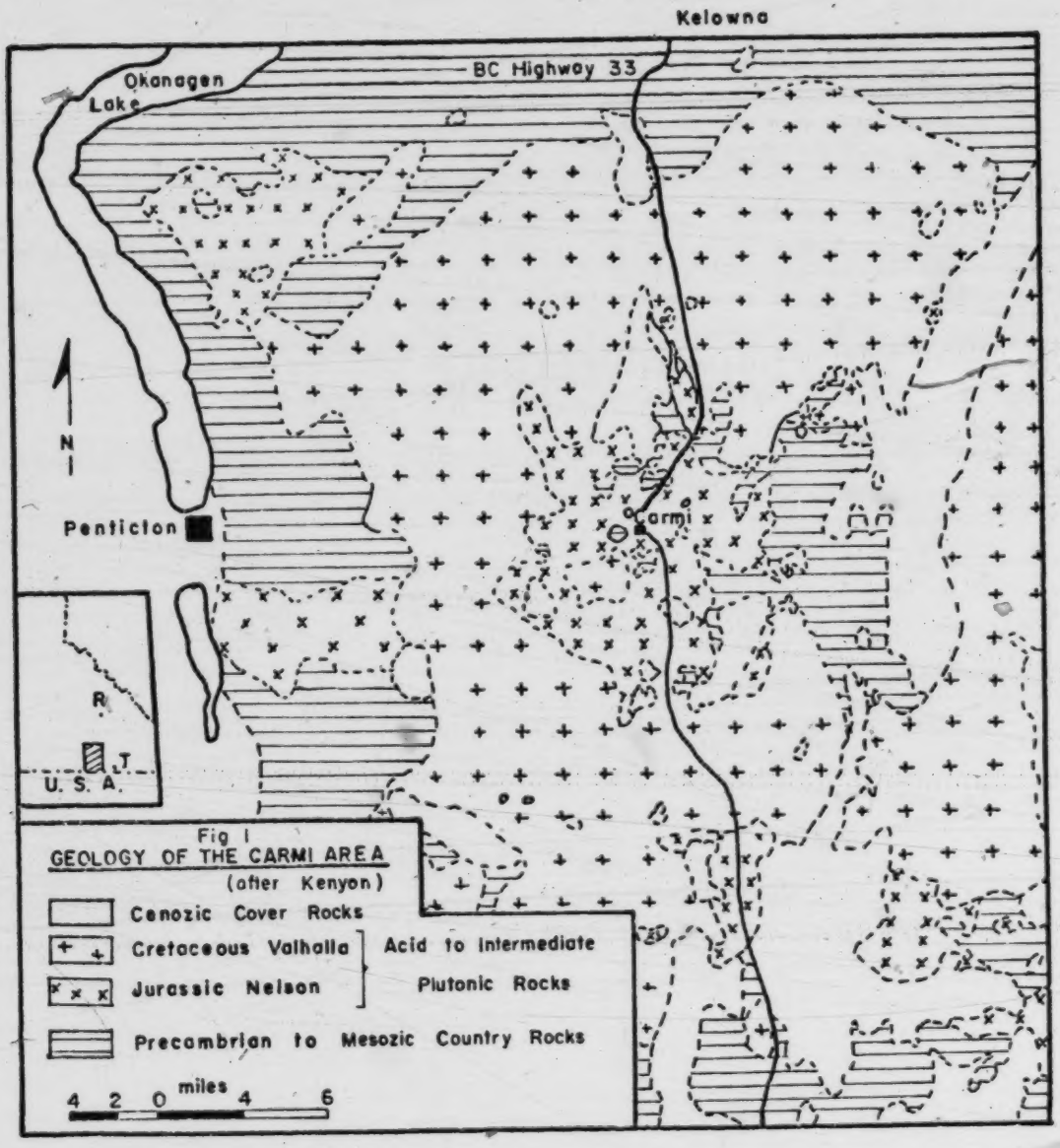


Fig 1
GEOLOGY OF THE CARMI AREA
(after Kenyon)

sphalerite, pyrite, magnetite, hematite and ilmenite. There are two main breccia bodies at Carmi; the western "Lake" zone and the eastern "E" zone. The study area was situated over the "E" zone, figure 2.

Physiography

The Carmi area is located within the Okanagan Highlands of the Interior Plateau (Holland, 1964).

The study area lies on the eastern side of a 1365 m high plateau between 1220 m and 1140 m above sea level. In the eastern part of the area, the ground slopes off steeply to the east. The western part is flat or gently undulating. There is a steep sided, east-west valley in the eastern central part of the area. "Showing" creek flows all year round in this valley. A poorly drained, almost marshy area extends to the west of the valley.

The area is covered with ice-deposited till which was transported from the northwest (B.C. Atlas of Resources, 1956). The depth of overburden varies from zero feet, at the very infrequent outcrop cites, to 80 feet (24.5 m). Fig. 2 shows spot till depths at various drill hole localities. The till has a poor soil profile developed upon it which has been defined as mountainous podzol by the B.C. Atlas of Resources (1956). The "A-B" horizon contact is marked by a colour transition from dark grey to dark brown. Generally the soil contains numerous pebbles up to 5 cm in diameter. In areas of poor overburden cover, on the eastern slopes, the till contains large amounts of angular bedrock fragments.

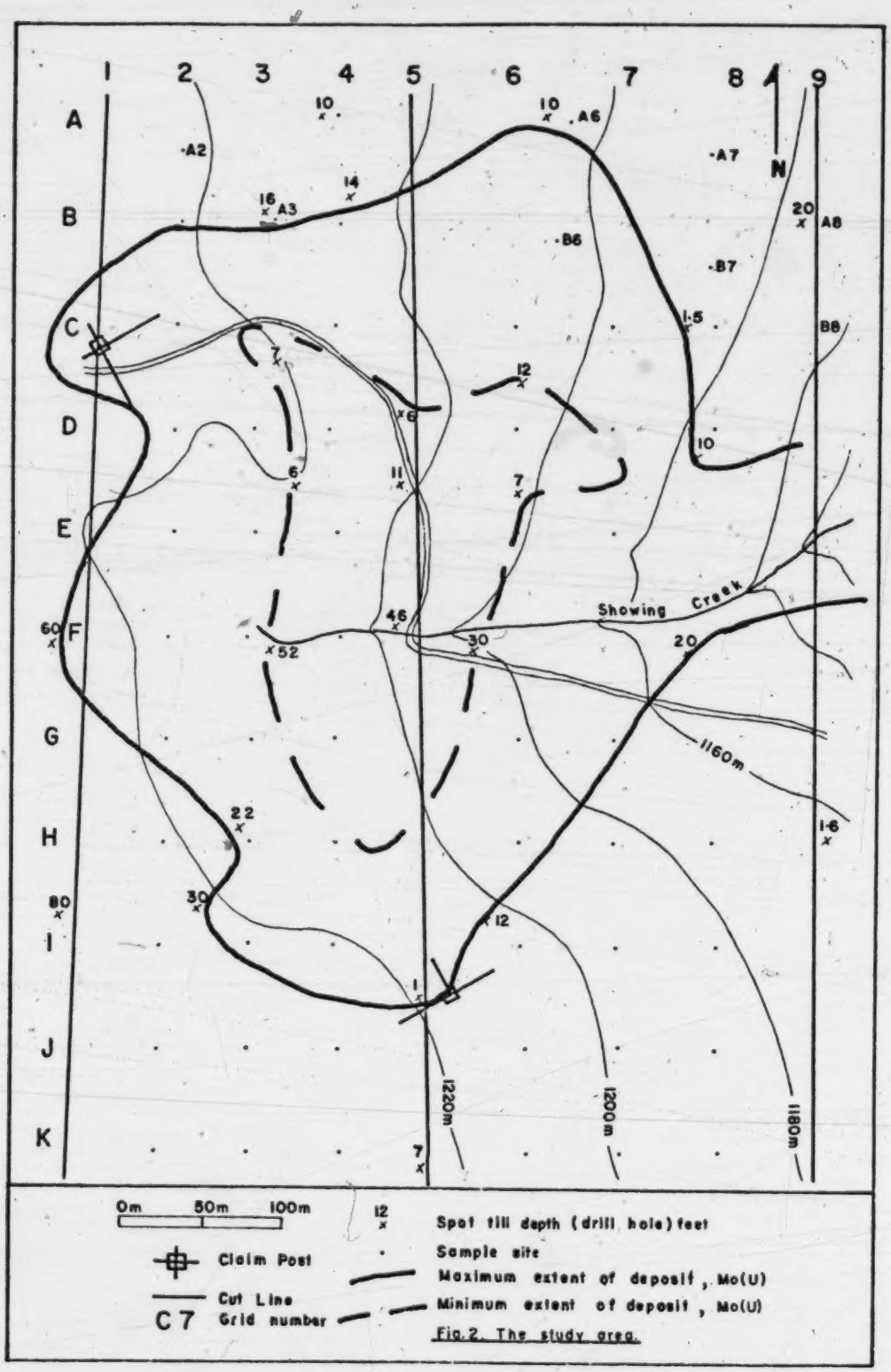


Fig. 2. The study area.

## Vegetation

Western Larch *Larix occidentalis* is virtually ubiquitous in the study area with Lodgepole Pine *Pinus contorta* and White Spruce *Picea glauca* much less abundant. The rest of the floral population consists of short grasses and several species of small deciduous bush. The area was burnt in the recent past so most of the trees are immature. In this area Lodgepole Pine has a height of between 2.5 m and 5 m and Western Larch between 2 m and 5 m. Western Larch has a deep system of lateral roots whilst the Lodgepole Pine has a deep tap root when young, which later develops into a moderately deep system of lateral roots (Dominion Forest Service of Canada, 1961). Some mature trees, of various species, survived the fire and stand over 20 m high.

Lodgepole Pine is almost completely absent from the wetter central part of the area. Western Larch is not present in the very wet Showing Creek region.

## Climate

Appendix 2 shows the measured values of the major climatic factors affecting this area. However, a micro-climate exists within the study area. Deciduous bushes grow in the more open areas, especially along roadsides and at cleared drill sites. This is probably due to the increased flux of sunlight available at these places. This factor, along with wetter soils, is probably why deciduous bushes rather than coniferous and deciduous trees predominate in the valley.

# CHAPTER 2

## BIOGEOCHEMISTRY THEORY

### Definition

There are two sciences involving the relationship between geology and plants, namely: *"Geobotany and Biogeochemistry"*.

*"Geobotany"* makes use of particular species and their vagaries, growing over particular rocks or ore types. A plant that is known to grow over a particular feature is termed an *"Indicator Plant"*; for example; the California Poppy *Eschscholtzia mexicana* which grows over Cu rich areas in the south western U.S.A. *"Geobotany"* does not involve any chemical analyses. Botanical and ecological observations are the most important factors in this science.

*"Biogeochemistry"* involves the analysis of a plant or parts of a plant. It is hoped that the plant takes up elements that are present in the substrate and that this uptake is in some way proportional to the substrate concentration of those elements. Certain plants can accumulate particular elements to very high levels. These plants are termed *"accumulator plants"*. *"Biogeochemistry"* offers several advantages and disadvantages, over soil geochemistry, in the search for mineral deposits.

### History of the Method

Credit for the introduction of the science of biogeochemistry has been assigned to Vernadsky, Vinogradov and Tklaich in the Soviet Union as well as to Brundin and Palmqvist in Sweden and England, all of whom

worked in the late 1930's (Brooks, 1968, 1972; Wolfe, 1971). Demarcay, in 1900, was the first to detect Mo in plants. Later, Dingwall, Mckibbon and Beans in 1934 and Beans, Eppson and Gilbert in 1935 did more work on plant Mo content (Cannon, 1964; Malyuga, 1964). The reason for biogeochemistry emerging in the thirties was due to the arrival of rapid analytical techniques in the form of emission spectrometry.

During the 1940's Vogt in Scandinavia and Warren and Delavault in British Columbia began systematic biogeochemical investigations. Warren and Delavault have been very active in this field and have published many papers containing valuable basic information on practical biogeochemistry. Hornbrook, Fortescue and Wolfe have taken over the advancement of Canadian biogeochemistry since Warren and Delavaults' retirement at the beginning of this decade. Cannon completed extensive practical work in relation to the Colorado Plateau U and V deposits during the fifties and sixties. Chaffee continues investigations in the U.S.A. today.

Brooks and his co-workers have had success in New Zealand and have advanced the science with their statistical applications since 1968 (Brooks, 1968).

The Soviet Union has always been a principal centre for biogeochemical research and practice with Layuga, at the Vernadskii Institute, as the main practitioner.

Both Brooks (1972) and Malyuga (1964) have published biogeochemistry text books. Malyuga's book contains much useful information but is poorly presented. Brooks' (op cit) book is excellent and can be considered the definitive work on the subject. Carlisle and Cleveland

(1958), in a shorter work, give an excellent review of methods.

Plant Physiology

Plants utilize a large variety of elements, including trace elements, in various quantities. The trace elements are mainly located within proteins and enzymes as shown below (Brooks, 1972). An over- or under-abundance of trace elements may cause serious problems for the plant. It seems likely that if any particular element is present in the substrate in an assimilateable form then plants growing on that substrate will contain that element even if only at the sub-ppb level.

Mo is found in the enzymes: nitrate-reductose (Mo flavoprotein) and xanthineoxidase ($C_5H_4N_4O_2+O_2$) (Bowen, 1966; Vinogradov, 1963) and metalloflavin enzymes (metal + flavin group) (Brooks, 1972) (formulae from Meyer, 1973). Sauchelli (1969) also notes that Mo is utilized in the synthesis of ascorbic acid which makes iron physiollogically available to the plant. Mo is probably the prosthetic group in ascorbic acid oxidase which acts on ascorbic acid (Levitt, 1974).

Not all forms of metal are in a form that can be assimilated by the plant (Malyuga, 1964). Hawkes and Webb (1962) and Cannon (1960, 1964) state that metals can be taken up by a plant when they are: in solution, in an exchangeable form adsorbed on clay and when combined with extruded-metalo-chelates,-citrates,-malates,-tartrates and -amino acids. Some *"converter plants"* take up an element in a form that is not available to other plants. When these die the element is returned to the soil in a form that can be assimilated by other plants.

Nutrient metals can get to the plant's roots in two ways according to Mitchell (1972; (i) by diffusion down a concentration gradient to the low concentration area at the root caused by adsorbtion at the root, or (ii) by the root growing into new areas because of depletion of the old area. This latter method is not believed to hold true by all workers (Mitchell, 1972).

Once the metal is in the vicinity of the root, it can be assimilated in many ways (Cannon, 1960, 1963; Hawkes and Webb, 1962). Metals can enter in solution, by cation exchange with the substrate and by combination with reagents exuded by the root which are then readsorbed. Hawkes and Webb (1962) also state that root tips reduce a high acidity, which may be due to the reaction:

$$CO_2 + H_2O \longrightarrow H_2CO_3 \longrightarrow HCO_3^- + H^+$$

However, this requires a high partial pressure of $CO_2$. It seems more likely that exuded humic acids are responsible for this root tip acidity. This can also liberate elements that are firmly bonded to clay particles. This acidity can also break down minerals to variable extents.

Barber, Holstead and Follet (1967) studied the soil/plant system in relation to Mo and concluded that element solution and root interception were the most important factors in Mo uptake and that diffusion along a concentration gradient was of minor importance. Stout and White (1959) discovered that Mo is ten times more readily assimilated in phosphate rich soil than sulfate rich soil.

According to Hawkes and Webb (1962) elemental uptake depends on the availability of the elements, the general requirements for plant nutrition and the particular chemical and biological effects of the

nutritional processes of individual species.

Bowen (1966), Hawkes and Webb (1962) and Cannon (1960, 1963) have summarized the processes that affect elements once they are inside the plant. The metal is absorbed throught the unicellular root tip, which is constantly being replaced as the root grows. Here it may be accumulated if it is present in toxic amounts, as in the case of lead, and hence impede the flow of other elements. Cannon (1964) does not think that this can happen since accumulation in the roots would result in a reverse concentration gradient draining that element away from the roots. It would be expected that those roots with better cation exchange properties would have higher concentrations. Elements are then transported up the xylem by diffusion to the aerial parts of the plant.

## Variations in Plant Elemental Content

Variable concentrations of an element appear in different parts of a plant because of the different ways in which individual elements are transported in the plant (Cannon, 1960). Also specific plant organs have dissimilar nutritional requirements. Siegel (1974) suggests that, in general, metal accumulation by trees conforms to the following increasing metal content progression: bark roots wood cones twigs leave/needles. Warren and Delavault (1955) discovered that tree tops or "leaders" may contain less metal than side boughs. For this reason care should be taken not to collect a disproportionate amount of leaders during a survey. In 1968 they reported that heartwood, bark and cones were not reliable sampling mediums. Warren,

Delavault and Fortescue (1955) also noted that lower and upper branches may not contain the same amounts of metal.

It is obvious, therefore, that only identical organs of one species should be compared during a biogeochemical prospecting survey. For example; Jack Pine 2nd year growth twigs (the growth due to the previous year's growing season). The same aged samples are necessary since metal uptake can vary from year to year (Warren, Delavault, and Fortescue, (1955)).

In contrast Warren and Delavault (1957) proposed that since many species showed only slightly different Co contents and that they showed little variation in the previous three years, any species could be sampled at any site. However, their published Co content values were very low, only a few ppm Co, and as such minor differences could indicate mineralization. These minor differences would very likely be within the range of concentration differences for the different species. Also Malyuga (1958) discovered that various species of herb collected the same amounts of Mo at the same sample site and could therefore be substituted for each other.

Beus and Grigorian (1977) state that a tree's concentrating power can sometimes vary with overall tree age. That is an older, larger tree may not contain the same amount of metal as a younger, smaller tree of the same species at the same site. Therefore, trees of the same size should be sampled. Wolfe (1974, 1976) disagrees with this observation.

In addition, to these variations caused by internal processes, there are variations caused by external factors for example; avail-

ability of sunlight and rain, soil pH, terrain, proximity to open water and many others (Hawkes and Webb, 1962). One very important factor is the variation in element concentration through the growing season. For this reason sampling should be completed in as short a time as possible. Cole (1968) did work to find out which time of year was best for sampling Pb and which was best for Zn. However, concentrations tend to remain stable through the winter.

Warren and Delavault (1955) and Malyuga and Petrunina (1961) both indicate that biogeochemistry will work in areas of permafrost terrain although care should be taken when comparisons are made with permafrost-free areas.

Care should be taken during the analysis of a set of data to ensure that any anomaly due to these external factors if recognized as such and not as an anomaly due to an underlying mineral deposit.

When all these factors are taken into account it should be realized that information gathered from an orientation survey is necessary for each new area before it can be properly prospected.

## Exclusion Mechanisms

Usually, increasing amounts of an element in the soil are reflected by increasing amounts in the plant. However, this process sometimes breaks down and the plant does not take up the element in a 1:1 relationship as described by Brooks (1972), Hawkes and Webb (1962) and Marmo (1953). This may be due to the plant taking up only that optimum amount of an element it requires for nutrition. This feature has been termed the "Exclusion Mechanism" by Brooks (1972). Exclusion mechanisms

often break down at very high soil concentrations whereupon the plants take up correspondingly large amounts of an element. Figure 3 shows exclusion mechanisms operating on two of the three elements plotted.

If at all possible, plants with no, or, very high concentration physiological barriers should be chosen for sampling (Kovalevsky, 1976). In 1974 the same author stated that 16% of the plants growing over Siberian ore deposits were Mo barrier-free and 65% had a very high barrier. This is what makes Mo biogeochemistry a potentially successful exploration tool.

Trace elements, such as Cu and Zn, that are very important to a plant's health, are quite often affected in their uptake by several external factors, for example; variations in sunlight and rainfall. Therefore, when considering Cu biogeochemistry it is a good idea to plot Cu:Zn ratios for plant organs so that variations in the external factors will be counter balanced by the Zn values thus leaving anomalies that are due only to Cu mineralization (Beus and Grigorian, 1977). Worthington (1955) describes the successful indication of the ore body at Shawangunk Mine, New York using a Cu:Zn ratio in White Birch twigs.

## Biogeochemical Provinces

Vinogradov (1963) introduced the concept of *"Biogeochemical Provinces"*. These are areas where soil and climate conditions are generally the same and where it is hoped that the results of one orientation survey will have wide ranging application.

Biogeochemical Provinces may be defined in a second manner, namely: regions where the vegetation has anomolously high, or low, amounts of a

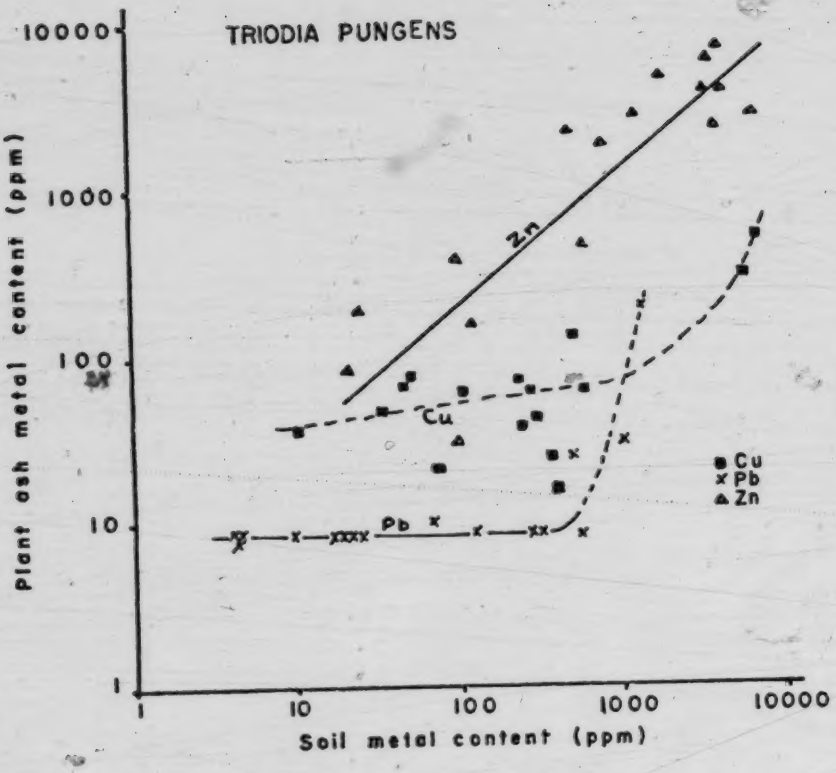


Fig. 3. Exclusion Mechanisms.

(Brooks 1972)

(The exclusion mechanism is shown by the horizontal or near horizontal lines.)

particular element or elements. An example would be the cattle molybdenosis areas due to higher concentrations of Mo in a particular pastural region as reported by Barshad (1948), Robinson and Dever (1956) and Sauchelli (1969).

This idea has not received wide acceptance in the West, probably because it seems unlikely that large areas, on the Soviet scale, can be defined as having similar features.

Malyuga (1964) suggests that those provinces of the moderately dry steppes which have a continental climate, dark chestnut and chernozemic soils and xerophytic (shallow) roots should be prospected by biogeochemical soil (humus) surveys. All other areas should be approached by regular biogeochemical methods.

## Advantages and Disadvantages of Biogeochemistry

### Disadvantages

The main disadvantage of biogeochemistry is the variation in uptake that can result from a wide variety of physiological, climatic, and soil environment related factors. However, most of these factors can be realized and negated by systematic sampling.

It has been suggested by Brooks (1972) that works in biogeochemistry need to have a knowledge of many disciplines including botany, physiology and soil science. However, this author does not believe that this is necessarily the case since he has had no formal training in these sciences yet managed to complete this study successfully.

Warren (1962) claims that ashing (see Laboratory Methodology, Chapter 5) is a disadvantage because it is an extra step. However,

Brooks, (1972) refutes this by pointing out that in many instances soils have to be ashed to destroy organic, humic material before they can be analyzed.

Several workers have concluded that biogeochemistry did not work in their projects. In many cases the method was not used correctly in that sampling was not rigorous or plant organs that are known to be poor accumulators such as heartwood, were collected.

This worker discovered that the preparation of vegetation material prior to ashing is extremely time-consuming and monotonous. This preparation involves splitting the sample into needles and the various age twigs. However, this problem should be reduced considerably in an exploration programme since the orientation survey should have identified the one organ that constitutes the best exploration tool.

Advantages

Biogeochemistry is usually compared to soil geochemistry as a mineral exploration method since the plant usually gets its trace metals from the soil. Nevertheless, direct mineralization interception by acidic root tips must not be forgotten.

There are two major advantages that biogeochemistry has over soil geochemistry. The first is the great depth that phreatophyte (deep) roots can reach, sometimes contacting the mineral source itself. The second is the large amount of soil that a plant's root system samples. Kovalevsky (1976) estimates that lithological sampling is 100, 10 and 3 times as expensive as biogeochemical sampling at the 35 m, 4 m and 2 m depths respectively.

Biogeochemical sampling is much easier than soil sampling especially in areas of thick humus and intertwining root systems (Brooks, 1972; Quin et. al., 1974). In most cases species identification does not present a problem, especially after a little practice, thus unskilled samplers can learn to sample very quickly.

One of biogeochemistry's major advantages over all other geochemical methods is that it can still be carried out during the winter months. (Kovalevsky, 1976). Of course winter sampling of deciduous leaves and needles is not possible. Deciduous species identification is also somewhat more difficult in winter.

## Future Advances

The Soviet literature has made some vague statements implying that they are working on in situ plant analysis (Kovalevsky, 1976). No details have been published so far. If such a method does exist and could provide accurate analyses of the small amounts of trace elements in living vegetation, then biogeochemistry could well relegate soil geochemistry to a very minor position in exploration geochemistry.

Canney (1971) recognized anomolous Cu-Mo Balsam Fir, in Maine, by differences in the Fir's percentage reflected wavelengths. Since the Landsat I and II satellites are continuously relaying this type of information it would seem likely that reflectance work could become a very effective exploration tool.

Brooks (1968) has suggested using helicopters to sample densely vegetated areas from the air. It would seem, however, that this would be a very imprecise sampling technique with many errors and hazards involved.

# CHAPTER 3

## PREVIOUS WORK

### Mo Biogeochemistry in Canada

Hornbrook (1969) made a study of the Lucky Ship Mo deposit at Morrice Lake, 55 miles south of Smithers, British Columbia. This is an area of Alpine Fir and Lodgepole Pine growing at 3000 - 4000 feet above sea level on podzol developed over sand and gravel. 144 sample sites were chosen and samples were analyzed in a mobile spectrograph-equipped trailer.

Alpine Fir 2nd year needles were found to be equally as good as the "B" soil horizon in outlining the deposit. However, the plant material gave a large Mo contrast. Material was collected in 1964 and 1967 and was found to contain identical Mo levels, thus showing that exploration disturbances in the area, in the form of drilling and road building in between collections, had no effect on Mo uptake.

Hornbrook concluded that biogeochemistry was cheaper than soil geochemistry and had the added advantage of winter sampling feasibility.

In 1970, Hornbrook investigated the Huckleberry Mountain Cu-Mo deposit 28 miles south of the Lucky Ship deposit. This area is virtually identical to the Lucky Ship and he came to the same conclusions except that the 2nd year Alpine Fir twigs were better than the needles.

Warren and Delavault (1965) worked on the Lucky Ship deposit

and made the same discovery as Hornbrook except that they reported that Balsam Fir and not Alpine Fir outlined the deposit. Since Balsam Fir is an Eastern and Central Canadian species it seems likely that Warren and Delavault misidentified the species.

In the same paper Warren and Delavault reported that they took 1,000 samples of Lodgepole Pine, Balsam Fir and White Spruce at the Dorothy-Elizabeth prospect at Duckling Creek, British Columbia and found that 100 ppm Mo was the anomaly threshold.

Warren and Delavault (1965), Warren, Delavault and Cross (1966) and Warren, Delavault and Routley (1953) give a few values of Mo concentrations in trees. However, these values represent analyses of a small number of samples gathered at deliberately anomolous sites and as such their value is limited.

Boyle and Troup (1975) had to sample phloem at their Capoose Lake, British Columbia investigation site because the trees were very tall. Nevertheless, the phloem Mo values did give coincident anomalies with other investigation techniques.

Warren and Delavault (1965) summarize Mo biogeochemistry in British Columbia and conclude that 1st year growth contains most Mo. They add that biogeochemistry can outline the ore body but give only an approximate idea of the grade. They then go on to state that commercial deposits should have at least 250 ppm Mo while less than 50 ppm Mo indicates ground of no importance. This is not the case with the present findings of the Carmi study.

The only other Canadian Mo biogeochemical work has been carried out by Wolfe (1974, 1976) on the Setting Net Lake Mo-Cu deposit in

Kenora, Ontario. This Pre-Cambrian porphyry is covered by podzol on sandstone-derived tills. The Mo content of 2nd year twigs and needles of Black Spruce and Jack Pine all showed the anomaly. Wolfe surmised that Mo in Black Spruce 2nd year needles and the "B" soil horizon were the best sampling media. He also notes that the age and physical size of the trees, within broad limits, did not affect the outcome of the survey.

## Mo Biogeochemistry in the Rest of the World

The most noteable use of Mo biogeochemistry outside Canada has been in the Karmir-Kara mineralized area in Kadsharan, U.S.S.R. Malyuga (1958) and Malyuga et. al. (1959) described how several mines were discovered by using Mo biogeochemistry. Other successful applications of the technique have been reported by Baranova (1957), Brooks (1968), Brooks and Lyon (1966), Carlisle and Cleveland (1958), Chaffee (1977, a, b), Lyon and Brooks (1969), Malyuga and Ayvazyan (1970) and Marmo (1953). Lounamaa (1969) and Salmi (1967) noted high vegetation Mo values in Mo rich areas. Kontas (1976) claimed the method did not work. However, his studies were based on very few samples, in one case only four samples.

## World Biogeochemistry

Biogeochemistry has been used in many places and on many elements in the world. An extensive list of these appears in the bibliography. 90% of the reported biogeochemical works have proven to be successful to some extent. Most of these studies have been on Pb, Zn, Cu and Mo.

The rest include Ni, Au, W, B, U, V, As, Co and the REE.

CHAPTER 4

## FIELD METHODOLOGY

Under ideal conditions an initial trip to an area is desirable so that samples from different soil horizons can be taken for analysis, to find out which horizon contains most of the sought after elements. At the same time the vegetation species and their abundances should be observed so that their distribution can be ascertained. The species that will be sampled should be present at most of the sample sites.

A soil geochemistry survey had already been conducted at Carmi, by previous operators, who chose to sample the "B" soil horizon. It was observed that most of the holes dug for this survey merely scratched the surface of the soil, so that in fact, the "A" soil horizon had been sampled not the "B". The "B" horizon occurs betwen 35 and 50 cm down from the surface at Carmi.

In the first instance, the proposed sample area was toured and it was noted that two species of tree, Western Larch and Lodgepole Pine, are the prominent species of the area. On average these trees were 5 m high which was ideal for sampling since the branches could be reached without climbing the tree itself.

The bushes and deciduous trees were not suitable for this study since they have an impersistent distribution. The grasses were not sampled since it would have been necessary to collect over a large area, at each sample site, to get a sufficiently large sample. 100 g of twigs plus needles were sampled since several analyses were to be made. This study shows that 10 g of dry material of each organ are required to make analyses for four elements.

At the end of the initial inspection it was decided to sample Western Larch, Lodgepole Pine and take soil samples from the "B" horizon. The Lodgepole Pine needles are yellowish and very spindly at Carmi when compared to the specimens that grow on the University of Alberta campus. This may be due to the better growing conditions on campus. However, spindly growth and yellow needles are signs of Mo concentration (Cannon, 1960). Yellowing of the needles, or chlorosis, may also be due to low Fe content as a result of the antagonistic effects Cu and Zn have on Fe metabolism (Brooks, 1972). Millikan (1948) noted that Mo can decrease the chlorosis effect due to Fe deficiency. However Fe deficiency is unlikely since Fe is available due to the oxidation of pyrite at Carmi (Kenyon, 1978). The Western Larch trees always seemed to be healthy.

This study's sampling grid made use of the existing cut grid. Sample spacing was laid out at 50 m between sample sites east-west and north-south.

The process of collecting sufficient vegetation from two species, as well as a soil sample, from each site was very time consuming. Collection usually took 20-30 minutes at each site. Digging the soil sample hole took most time since loose rocks and large tree roots impeded progress considerably. They had to be removed or cut out of the way before the hole could be continued. Once the hole reached the "B" horizon, which was not always distinguishable, by a change of colour, from the "A" horizon, the material which had fallen down from higher up was removed and a sample was taken. It was decided to adopt a soil sample pattern which covered the grid and included

49 of the total 87 sample sites.

It was necessary to take the sample from all heights of the Western Larch tree in order to obtain a large enough sample and also in order to combat possible concentration differences with height. Western Larch trunks could be bent over easily but Lodgepole Pine could not. Samples were placed in cloth bags for transport.

The cloth bags allow the vegetation to dry out. This makes sample splitting at the laboratory much easier. However, twigs, should not be crowded into the bag since this will cause them to intertwine and, when dry, will make separation prior to splitting very difficult. This drying out also makes the deciduous Western Larch needles fall off the twigs which saves a splitting step.

Showing Creek, which drains to the east of the area flows in a steep sided gully. The gully sides do not have a good soil development. The small amount of soil present is usually confined to spaces between boulders. The gully also promotes a different floral pattern. Here the vegetation is generally shorter and greener. Small spruce, abundant deciduous, broad leaf trees and much more shrubbery are present. The very tall mature trees are absent. Since the gully sides are steeper and the floor is wet, deciduous trees thrive and are present to the exclusion of Western Larch and Lodgepole Pine. Lodgepole Pine seems to be less adaptable to change than Western Larch since it was absent at several sites on grid lines E, F, G, and H. White Spruce was sampled in this area in an attempt to back up the information gap created by the Lodgepole Pine absence.

CHAPTER 5

# LABORATORY METHODOLOGY

## Atomic Absorption Spectrophotometry

Atomic Absorption Spectrophotometry (A.A.S.) was chosen as the analytical method because it is rapid and can detect lower concentrations of elements than most other methods. Just recently it has become possible to analyze ash itself by gamma spectrometry after neutron activation in a SLOWPOKE reactor. However, this method is not yet suitable for Pb analyses, and, only small numbers of samples can be irradiated at one time.

A.A.S. works on the principal that "ground state" or unexcited atoms of a particular element will absorb specific radiated wavelengths from excited atoms of the same element. In practice a hollow cathode lamp with the cathode made of the desired element is used to supply the radiation. The argon gas in the lamp is heated and the ions excite the cathode. The outer electrons of the cathode's atoms are excited and move to a higher energy state. When they collide with other electrons they lose this energy which is emitted as radiation. A particular wavelength is isolated and passed through an acetylene/air or acetylene/nitrous oxide flame into which the sample, in solution, is aspirated. The flame breaks down the chemical bonds in the sample and puts the atoms into the "ground state" whereupon they absorb the emitted radiation. The more sample element present, the more absorption occurs and the less emitted radiation gets through the flame to

be measured by photomultipliers and an amplifying system on the other side. The result is given in the form of an analogue, digital or chart recording. Measurements are made relative to standard solutions (Brooks, 1972; Levinson, 1974).

Plant Material Analysis

The vegetation samples were first split into needles, first, second and third year growth twigs in the case of Western Larch, and into needles and first year growth twigs for Lodgepole Pine. The split samples were then washed thoroughly in tap water then rinsed in distilled water. This step is more important in sample areas which may receive windborne contamination from neaby mines, smelters or mine roads. However, Cole (1968) found no difference in concentrations between washed and unwashed samples in her Australian work. In the case of Carmi the nearest possible source of contamination is the Highland Bell Ag-Pb-Zn mine at Beaverdell. However, this mine is eight miles away and is not a source of Mo or Cu contamination but could be a Pb an Zn source.

The split and washed samples were then dried at 110$^{o}$C in air overnight before weighing. The weights of the dried vegetation were taken so that metal concentrations could be calculated relative to original plant weight as well as relative to ash weight. Malyuga (1964), Warren et. al. (1955) and this study shows that concentrations calculated on ash weight basis are more reliable.

The dried samples were then ashed in aluminum dishes at 450$^{o}$C for 10 hours in furnaces with a sufficient air supply to allow combustion.

Experiments with ashing times showed that 10 hours were required for complete combustion even though the plant material stopped glowing, after ignition, after 2 hours. The ignition temperature of 450°C was commonly used by previous workers and is low enough to prevent loss of metals by volatilization.

Problems were encountered with the ashing step due to a heat and air supply gradient across the furnace. This necessitated the reburning of some samples which had turned to charcoal during the initial 10 hour combustion.

Aluminum pie dishes (Alcan brand, 7 inch size) were chosen as the only suitable containers which could be used since they are large enough to hold the large volumes of dried vegetation involved. They are cheap and can be handled shortly after removal from the furnace since they have a high heat transfer rate. A plate was analyzed by A.A.S. and was found to contain 20 ppm Mo, 250 ppm Cu, 1150 ppm Zn and no Pb. The plates were examined after ashing and showed no signs of destruction. The ashes were brushed from the plates using a soft bristled paint brush. It is assumed that there was no contamination of the samples from the aluminum plates.

After ashing, the samples were subjected to a hot acid attack in teflon beakers prior to analysis on a Perkins-Elmer 503 atomic absorption spectrophotometer. Initially 1 g of Larch needle, Pine needle and Pine twig ash, and all of the Larch 1st, 2nd and 3rd growth twig ash (0.2 g - 0.3 g) were used. Later only 0.3 g of Larch needle and Pine needle and Pine twig ash were used.

These ashes were wetted with distilled water, dissolved in 3 ml

HF and 10 ml conc. $HNO_3$ and then evaporated. The residues were then dissolved in 3 ml HCL and 10 ml conc. $HNO_3$ and evaporated. The residue was then dissolved two more times in 10 ml conc. $HNO_3$ to ensure that all the other acids had been removed. Finally the residue was taken up in 10 ml of 10% $HNO_3$. This solution was then aspirated into the A.A.S. flame to determine Mo, Cu and Pb concentrations. This solution had to be diluted by a factor of 25 for Zn analyses since A.A.S. is very sensitive for Zn and plant material has a very high Zn content.

Many of these final solutions still contained organic material. It was for this reason that such a strong acid attack was used. Previous workers have used a simple nitric acid leach and state that their ash dissolved. They do not say whether the ash dissolved completely. This organic material would probably not remain if the original plant material had been ashed at higher temperatures. However, higher temperatures would have resulted in loss of metal by volatilization. More complete combustion may occur if the samples are ground before ashing. Warren and Delavault (1949) have pointed out that contamination from the grinding mill is very probable.

It was assumed that the ferocity of the hot acid attach was sufficient to extract all the metal from this organic material. To test this assumption, organic residue from the final solution was ashed in platinum ware and re-analyzed by A.A.S. This analysis showed that there was no Mo, Zn or Pb and only trace Cu. It was assumed, therefore, that no metal was left in this organic residue.

When the samples were aspirated into the flame, the flame turned

orange indicating that Na and K were present. To check that this change of colour had no effect on the analyses, some sample solutions were spiked with standard solution and analysed. The spiked solutions' theoretical concentrations and measured concentrations were identical indicating that the change of flame colour had no effect on the analyses.

Analytical Errors

Reagent blanks were run with every batch of samples so that any metal content due to the reagents could be monitored. Pb was the only metal that showed up in these blanks, always in concentrations of less than 0.2 ppm Pb in the final solution. Corrections were made for this error whenever it occurred.

In A.A.S. analysis, sample concentrations are calculated relative to standard solutions. Therefore, it is important that the standard and sample solutions be as similar as possible for example, a difference of one order of magnitude in the acid concentration percentage can reduce the absorption of Pb by 20%. Both sample and standard solutions were made up to 10% $HNO_3$.

Mo absorption can be suppressed in the A.A.S. flame if Ca is present. This effect can be reduced by adding Al or Na. The Mo standard solutions have Al added. The vegetation samples already contain Na as well as K ions as shown by the orange A.A.S. flame. Since all the sample solutions were prepared in the same way, any systematic errors should have been the same throughout and can therefore be ignored.

The analytical sensitivities of the A.A.S. method on the sample solutions were 0.1 ppm Mo, 0.1 ppm Cu, 0.1 ppm Pb and 0.05 ppm Zn.

## Soil pH - Eh Measurements

Soil samples from sample sites A5, B5, C5, D5, E4, F5, G5, H5, I5, J5 and K5 were used for pH - Eh measurements to be used in conjunction with Eh-pH diagrams for the various elements.

50 g of -12 mesh soil was mixed with 50 ml of distilled water. The mixtures were stirred occasionally for one hour. The pH measurements were made on a Radiometer pH meter 26 with a glass electrode (Levinson, 1974).

Eh measurements were made on the same mixtures using a Fischer 520 digital pH/ion meter with an Orion platinum redox potential electrode. This sytem requires that a constant of 241 mv be added to the measured readings since the readings were made relative to a calomel electrode instead of hydrogen cell. The measurements were made at $20^{o}C$ and are given in Table 1.

## Soil Analysis

All the soil samples were sieved to obtain the -80 and 40-80 mesh fractions. Samples A5 - J5 were selected for optimum size fraction and analytical technique determinations. 1 g each of the -80 and 40-80 mesh fractions was mixed with 20 ml of hot, conc. $HNO_3$, allowed to digest for 48 hours and then evaporated to dryness. The samples were then made up to 10 ml in 10% $HNO_3$. Cholach (1969) showed that this method leaches 70%, 50% and 45% respectively of the total Pb, Cu and Zn in the soil. The method gives very reproduceable results.

A further 1 g each of the same samples was mixed with 20 ml of cold, 5% $NH_4Cl$ solution and allowed to stand for 24 hours. The solution was then filtered, evaporated and made up to 10 ml. This

| | pH | Eh(mv) |
|---|---|---|
| A5 | 6.05 | +490 |
| B5 | 5.90 | +510 |
| C5 | 4.90 | +535 |
| D5 | 6.15 | +470 |
| E4 | 6.20 | +500 |
| F5 | 5.95 | +510 |
| G5 | 5.90 | +520 |
| H5 | 5.25 | +545 |
| I5 | 5.60 | +500 |
| J5 | 6.10 | +470 |
| K5 | 5.65 | +500 |

pH range: 4.90 - 6.20
average: 5.80

Eh range: +470 - +545mv
average: +505 mv

Table 1. Soil pH/Eh Measurements

cold extraction technique was used to determine the amount of readily available metal in the soil system. If an acid had been used, absorbed metal may have been extracted from organic material in the soil.

The results of this experiment are given in Appendix 3. The cold extractable technique did not show any Mo or Pb and showed mostly unmeasureable trace amounts of Cu. This would seem to indicate that there is no readily available Mo, Cu, or Pb in the soil. The Zn values were meaningless due to high Zn contents in the blanks.

The hot acid leach showed that, except for samples D5, E5, G5, I5 and J5, the -80 mesh fraction contains more Mo than the 40-80 mesh fraction. For Cu, Zn and Pb the -80 mesh fraction showed higher concentrations than the 40-80 mesh fraction, except for J5.

The hot acid leach method applied to the -80 mesh fraction was chosen as the best method to analyze the rest of the soil samples. All the soil analyses are listed in Appendix 4.

Analytical Errors

Since brass sieves were used on the soil samples there was a chance that the samples might have become contaminated with Cu and Zn. Some quartz beach sand, used for cleaning platinum ware, was sieved and put through the same analytical technique and showed that there was no contamination due to the sieves.

$NH_4Cl$ was added to the standards used in the analysis of the cold extractable metal. A comparison of standards with and without $NH_4Cl$ added showed that the regular standard had 1.06, 1.09, 1.19 and 1.12 times higher absorptions for Mo, Zn, Pb and Cu respectively than the standards containing $NH_4Cl$.

Uranium Analysis

Kenyon (1978) reports the presence of U in the form of Brannerite at Carmi. However, the U mineralization is limited and confined to the northern part of the mineral deposit. Since U is one of the "easy" elements in biogeochemistry (Brooks, 1972) it was hoped that U could be determined in this study.

It was not possible to analyze for U by A.A.S. since the sensitivity of the lamp was not good enough. Other methods were investigated, namely:

(i) Scintrex UA-3 Uranium Analyzer

This machine was considered since it offers a rapid, easy method for analyzing large numbers of samples. Robbins (Scintrex brief), described the machine and its use. The method requires that approximately 7 ml of sample solution plus 0.7 ml of reagent (FLURAN) be placed in a quartz cell. The analysis takes 10-20 seconds and a reading is given on a standards calibrated scale.

The analyzer works on the principle that the soluble uranyl ion and uranyl-complex forms, fluoresce characteristically. Organic matter in the sample solutions will also fluoresce but in blue wavelengths as opposed to the green of the uranyl species. Filters are used to help block the organic emissions. The ultraviolet radiation used to excite the solution is made to last for a few nanoseconds by using a laser power source. Since the organic fluorescence lasts for nanoseconds whilst the uranyl complexes phosphoresce for a much longer time, the phosphorescense is not measured till after the organic component has ceased.

$Fe^{2+}$ and $Mn^{2+}$ tons can severely quench the uranyl fluorescence.

For this reason a reagent (FLURAN) is added to the sample solution in the ratio of 1:10. This reagent suppresses the quenching effect of $Fe^{2+}$, $Mn^{2+}$ and organic materials. However, it is necessary to keep the concentrations of $Fe^{2+}$ and $Mn^{2+}$ ions below 8 ppm and 1.5 ppm respectively. At these concentrations a 20% reduction in sensitivity of the method, results.

Samples of Western Larch and Lodgepole Pine were analyzed by A.A.S. and found to contain 150 ppm Fe and 690 ppm Mn in the case of Larch and 75 ppm Fe and 560 ppm Mn for Pine in the sample solution. Brooks (1972) gives the average plant ash content of U as 600 ppb (18 ppb in the sample solution). Therefore the 10:1 dilution necessary to bring the concentration of U within the 1-10 ppb U range of the instrument would still leave 15 ppm Fe and 69 ppm Mn in the Larch samples. Such levels would have a very serious quenching effect upon the U. fluorescence.

Ways of removing the Fe and Mn or U from the solution, involving ketone reagents or ion-exchange columns, were investigated but would have required considerable time in treating each sample. For this reason it was decided that the Analyzer, whilst having potential for solutions with low Fe and Mn concentrations, was not suitable for plant ash U analysis.

(ii) Fission Track Analysis

This process requires that the sample be irradiated in a nuclear reactor. Neutrons from the pile bombard the U nucleus which splits into two particles which move with great force and impinge on a plastic chip causing damage tracks to be made which can be counted after etching.

Various plant samples growing over the uraniferous part of the ore body were chosen to be analyzed. Approximately 1 ml of diluted solution used for Zn analysis on the A.A.S. was put in a small P.V.C. phial along with a Lexan plastic chip (1 cm x 0.5 cm). This phial was hermetically sealed with a soldering iron and, along with another small phial, was placed in a larger phial called a "rabbit". The "rabbit" was also hermetically sealed.

The samples were irradiated in a SLOWPOKE reactor for 2,000 seconds at $10^{12}$ neutrons/$cm^2$/s. After irradiation the samples were allowed to reach safe radiation levels (3 days). They were then opened and the chips placed in 6.5 N NaOH, at 65°C for 40 minutes, which etched the chip. The chips were removed and washed to halt the etching process. The tracks should then have been counted, under x 250 magnification, and compared to a standards graph.

However, the samples showed only one or two tracks on some chips and no tracks on others. When compared to a graph relating number of tracks to U content in ppb, the samples plotted below the lower sensitivity level (5 ppb U) of the system.

(iii) Delayed Nutron Activation

5 ml of the diluted sample solutions of 36 samples were evaporated and the residues (approximately 0.01 g) sent to Atomic Energy of Canada Ltd. in Ottawa for analysis. All the samples were reported as less than 0.1 ugU in each sample. That is the U content was below the system's detection limit for the mass of sample supplied.

After considering all these analytical methods it can be concluded that the vegetation samples at Carmi do not contain any measureable quantities of U.

# CHAPTER 6

## SOIL GEOCHEMISTRY

The minerals of importance, at Carmi, which are available for oxidation and transportation include; molybdenite, chalcopyrite, sphalerite, brannerite, pyrite, magnetite, ilmenite and minor calcite (Kenyon, 1978). Ag-Pb veins are also known in the region especially at Beaverdell. In this study, Mo, Cu, Zn and Pb were ascertained because of the presence, or assumed presence in the case of Pb, of their sulfides. The lack of suitable analytical techniques, plus the low contents of absence of U in the vegetation precluded the analysis of this element in soil. V is often associated with U, (e.g. sandstone-hosted U(V) deposits) so a number of samples were analysed for V, however, no V was found. Re is usually included in the molybdenite structure. In fact this mineral contains more Re than any other mineral, sometimes up to 1.8% (Klasov, 1966). Brooks (1972) indicates that the average Re content of plant ash is 0.005 ppm. Therefore Re was not analyzed in plant or soil samples.

The presence of pyrite is important because when it oxidizes, sulfuric acid and iron sulfaate are produced which are instrumental in the destruction of other minerals. The pyrite at Carmi does show leaching effects. The presence of mobile iron, indicated by iron staining from the oxidation of magnetite to goethite, (Kenyon, 1978), is important in plant physiology and is discussed under "Field Methodology, Chapter 4". Fe is also necessary for the formation of ferrimolybdite, $Fe_2 (MoO_4)_3 \cdot 7 H_2O$. Minor calcite is present and is a

source of carbonate which would increase the pH of the secondary environment and have a pronounced effect on metal solubilities as will be seen below. However, since there is not much calcite present, and the average measure pH of the area is 5.8 carbonate would not seem to be an important factor in this system.

Kenyon (1978) reports that surface rock samples have 0.1% - 0.2% total Mo but only 0.02% - 0.05% molybdenite, which indicates weathering and reformation of Mo minerals. The rock surface is usually weathered to a depth of a few centimeters. Oxidation can penetrate approximately 9 m along fault and joint surfaces where goethite, occasional malachite and dendritic manganese hydroxide are present.

Molybdenum

The measured Eh and pH of the soil ranges from +0.470 to +0.545 volts and 4.9 to 6.2 respectively. The average values are +0.505 volts and 5.8. Figure 4 is the Eh/pH diagram for Mo and shows that that part of the soil environment with pH less than 6 favours the production of relatively immobile (easily captured) $HMoO_4^-$ whilst pH's greater than 6 favor mobile $MoO_4^{2-}$ production. The sites of mobile Mo complex formation will lose their Mo, whilst the immobile sites will retain it. This is shown by Figure 5 which shows a north-south profile across the sample grid. It also shows a soil concentration at D5 in what should be a mobile environment, pH 6.15. However, this is an outcrop area where the soil is poorly developed and very thin. It, therefore, probably contains part of the weathered outcrop itself analogous to a "C" soil horizon. This results in a high soil Mo content at this site. The

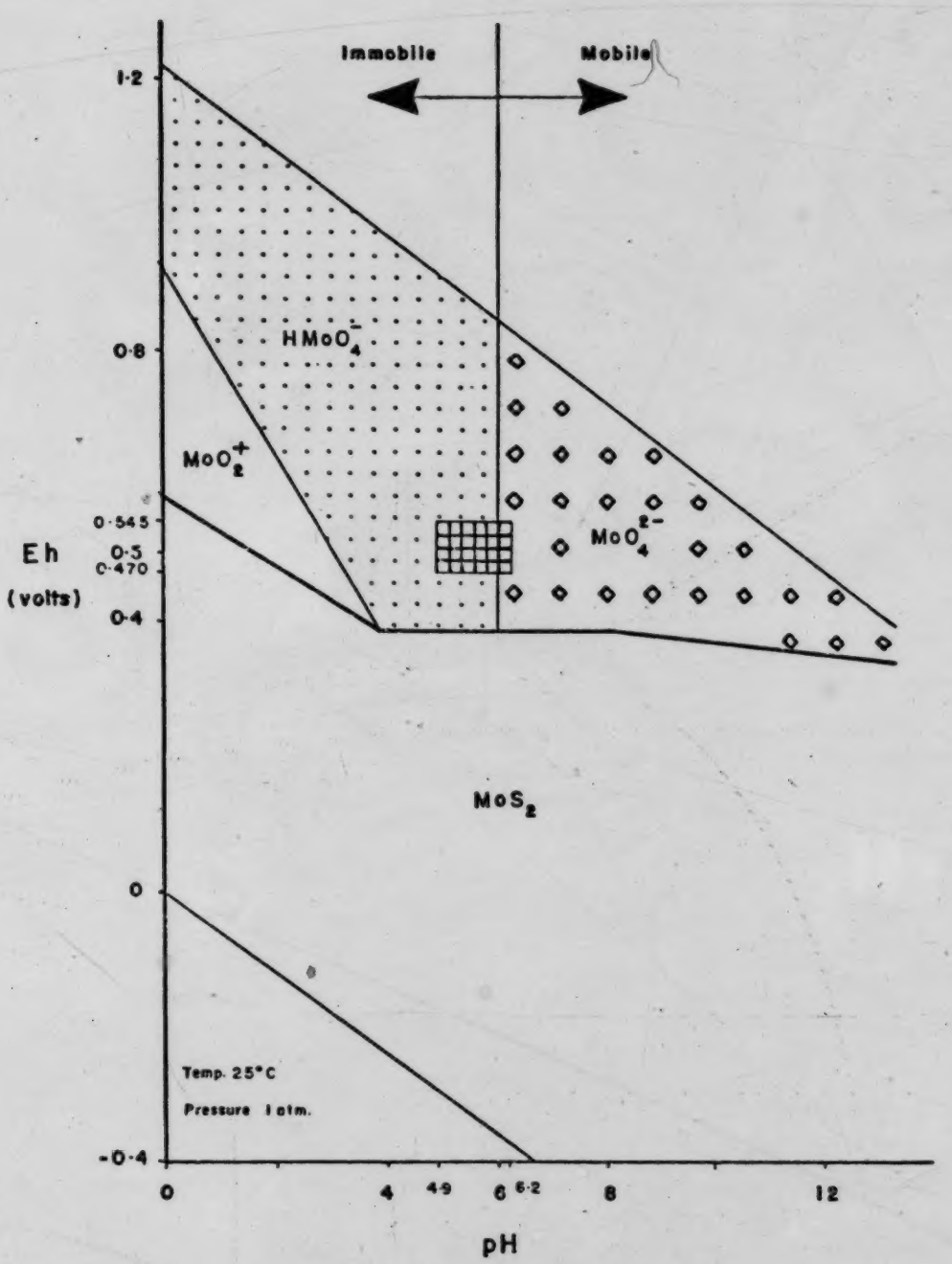


Fig.4. Eh/pH diagram for the molybdenite – water system.
(Levinson 1974)

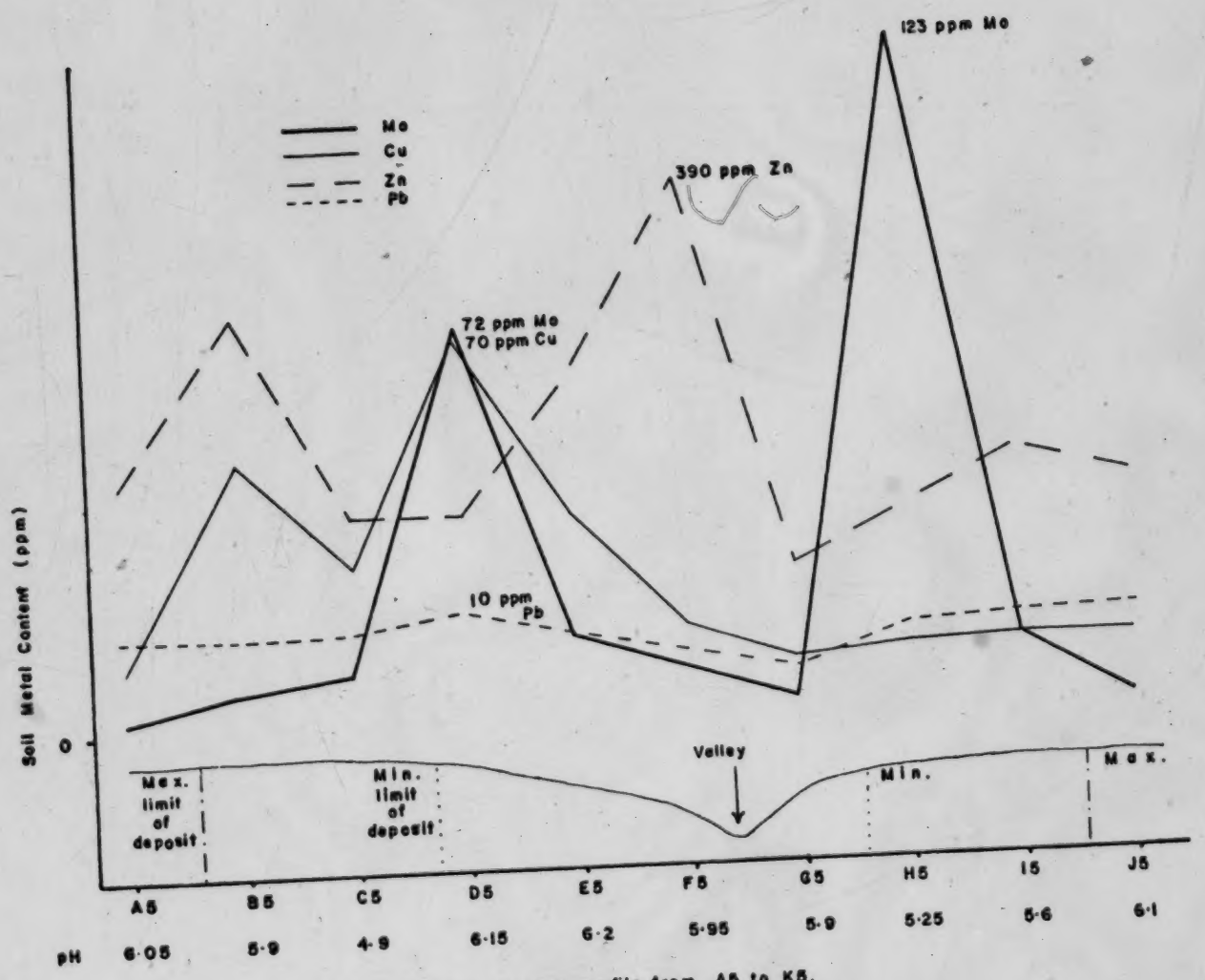


Fig. 8. Soil metal content profile from A5 to K5.

lack of a peak at the low pH sites B5 and C5 is due to these sites being positioned away from the ore body.

Pokalov and Orlov (1974) consider that Mo mobility is determined by the climate and sulfide mineralogy, and that Mo loss is greater in arid climates. Mikhailov (1962) hypothesises that in areas of high relief and poor soil formation, as at Carmi, 5% of the total Mo is in a soluble form. Oxidation of molybdenite is not only dependant on climate, relief, Eh and pH but also on the activity of *Thiobaccilus Ferroxidans* which attacks molybdenite for the sulfur content (Barakso and Bradshaw, 1971).

There are several secondary Mo complexes that can be formed from oxidation. Pokalov and Orlov (1974) suggest that molybdenite and iron sulfate, from pyrite, react with sulfuric acid to form immobile ferrimolybdite. Kenyon (1978) reports the presence of occasional yellow/orange ferrimolybdite at Carmi. Malyuga (1964) suggests that $MoO_2.SO_4$ is the mobile Mo form resulting from the oxidation of molybdenite in the presence of water. Mo can be absorbed by clays and Fe, Mn and Al hydroxides.

Re is more rapidly dissolved and removed, as perrhenic acid, than Mo during molybdenite oxidation. Humid areas are characterized by near complete Re removal. There is much less Re in the secondary Mo minerals of an oxidation zone than the molybdenite of that area (Klasov, 1966). It is not known whether this ease of Re solution means that plants growing in such an area will contain relatively high amounts of Re or whether the Re is immediately flushed from the area. However, it seems likely that in an ongoing molybdenite oxidation area, Re will

be continuously going into solution and hence be continuously available for plant uptake.

Copper

Figure 6 shows the Carmi range of Eh and pH plotted on a Cu Eh/pH diagram. Chalcopyrite-pyrite and chalcopyrite-magnetite assemblages are unstable under the local conditions. Their breakdown releases cupric ions into the ground water system and allows hematite to form. The arrow on figure 6 indicates the decreasing stability of Cu with increasing pH. Figure 5 shows only one Cu peak in the vicinity of D5 where mineralized outcrop is being continuously weathered and is supplying large amounts of Cu to its immediate surroundings. The profile does not show the expected peak distributions with higher pH.

Zinc

Garrels (1954) states that when sphalerite is oxidized, Zn becomes mobile and is generally removed from the sulphide locality. Rankama and Sahama (1950) think that zinc sulfate and zinc chloride are formed, and since they are mobile, Zn is transported in this form. The Zn profile on figure 5 shows a pronounced peak in the valley area. This peak is probably due to a gathering of these mobile forms.

Lead

No Pb minerals have been found at Carmi and the Pb soil content is average. Pb is a very immobile element and forms relatively immobile anglesite ($PbSO_4$) in most oxidation zones. Pb ions do not

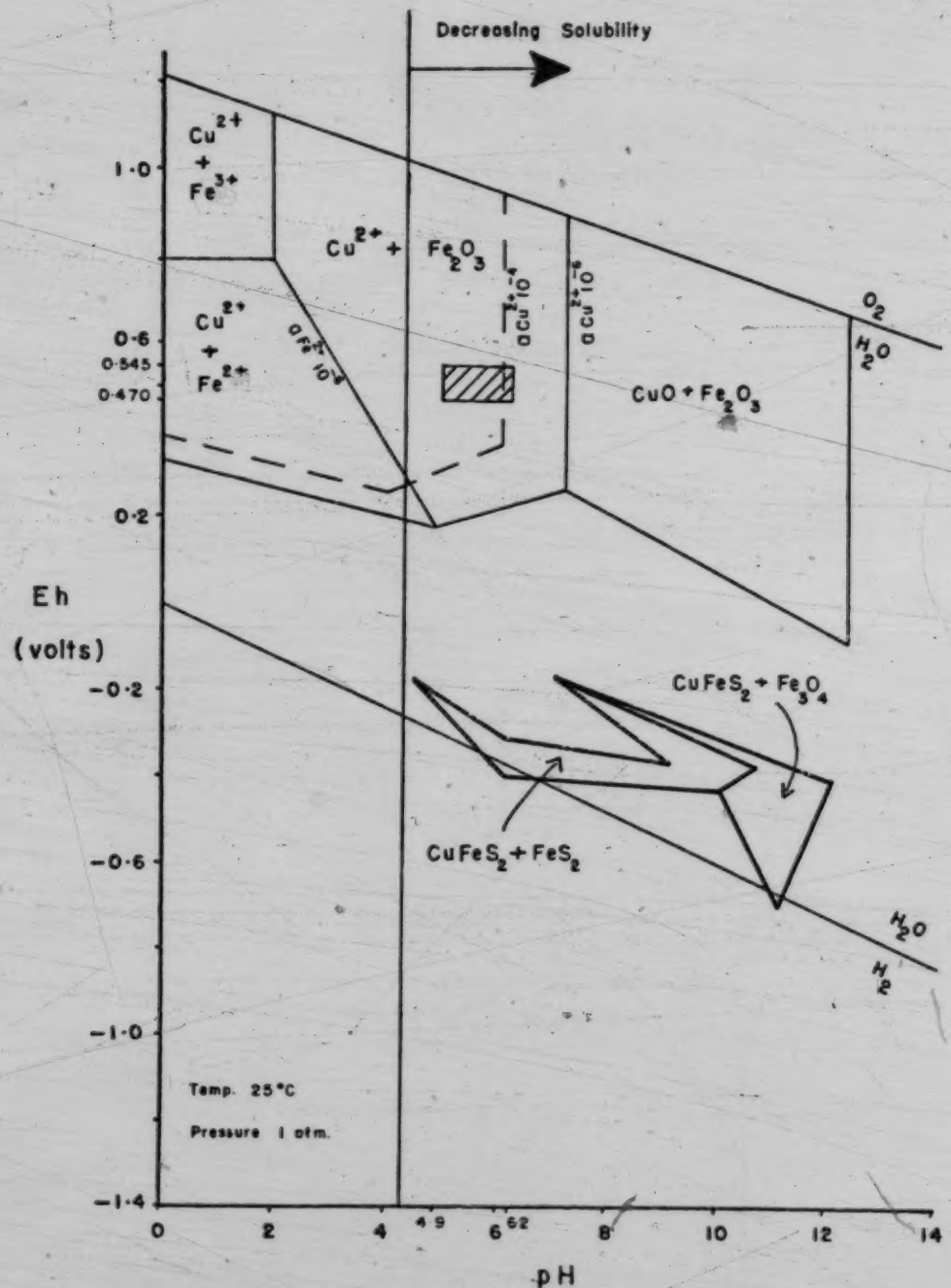


Fig. 6. Eh/pH diagram for the system Cu Fe S O H

(Garrels and Christ 1965)

become mobile until the pH drops below 1.0 (Garrels and Christ, 1965). The Pb profile on figure 5 is fairly flat indicating no Pb mobilization. It would appear that Pb maintains a constant, average value within the study area.

Uranium

Kenyon (1978) reports that brannerite ($UTi_2O_6$) is the U mineral at Carmi. Eh/pH diagrams for brannerite, in particular, are not available. $UO_2OH^+$ is formed in the U - $O_2$ - $H_2O$ system under this study's range of Eh and pH conditions. If the effect of atmospheric carbon dioxide is included then Rutherfordine ($UO_2CO_3$) is found to be stable as well. The inclusion of V and K in the system sees the formation of carnotite ($K\ UO_2\ VO_4$) (Hostetler and Garrels, 1962).

Therefore it would appear that U, in the form of $UO_2OH^+$ is available for plant uptake at Carmi. However, the sporadic amounts of brannerite present, preclude any wide spread U availability to the vegetation.

CHAPTER 7

# TREATMENT OF DATA AND CONCLUSIONS

## Vegetation

The raw data apertaining to vegetation are presented in Appendix 5.

In general the Mo content of Lodgepole Pine needles and twigs is higher than Western Larch twigs which is in turn higher than Larch needles.

Both Cu and Pb follow the succession: Pine and Larch twigs $>$ Pine needles, $>$ Larch needles.

Zn is highest in Pine twigs and needles, next highest in Larch twigs and lowest in Larch needles.

The elemental content of various organs was plotted against their corresponding soil value to determine if any exclusion mechanisms were operating (Brooks, 1972). Only the Mo content of all the organs of Larch and Pine showed an increasing Mo content with increasing soil content. The other elements did not show this relationship, figure 7. Therefore, it was deduced that exclusion mechanisms, or, in the case of Pb, some other factors were operating. The soil/vegetation graphs for Pb show an almost vertical straight line association with many vegetation concentrations for the same soil concentration. This may be due to different forms of Pb being available to the plant depending on local pH conditions combined with an exclusion mechanism since Pb is a very toxic element.

The Mo soil/vegetation graphs do not show perfect 1:1 correlations.

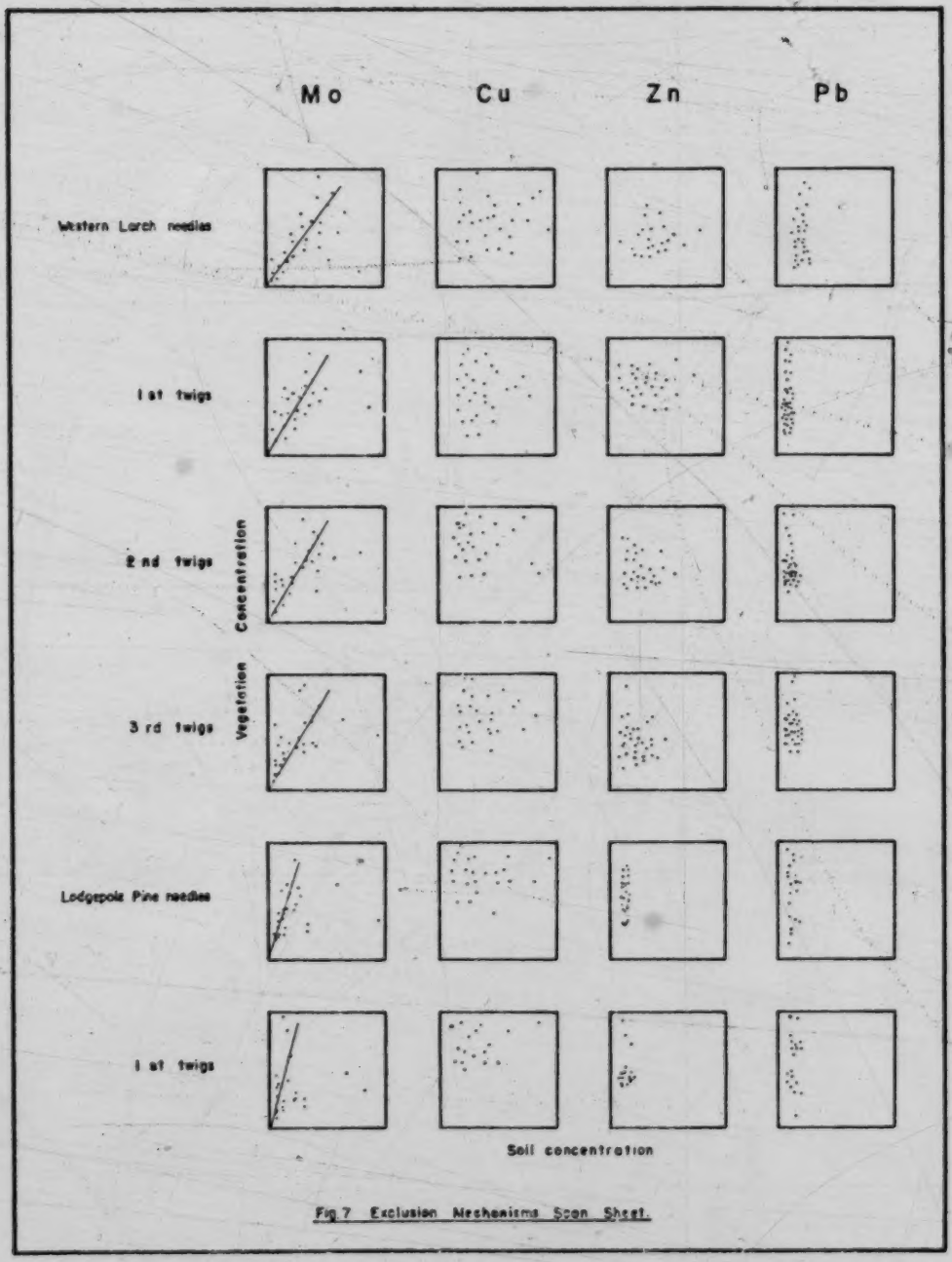


Fig 7 Exclusion Mechanism Scan Sheet.

It is felt that these graphs reflect higher Mo concentrations below the sampled soil horizon, perhaps the mineral bearing surface itself.

Background and threshold values were then calculated using two methods. The first was the histogram method of Cholach (1969). The second was the cumulative frequency/concentration method of Tennant and White (1950). Both methods are for use in cases where background and anomolous populations are mixed. Combining the two methods gave a reasonable value for the two terms. Table 2 gives the background and threshold values as well as concentration ranges for Mo.

The data were then contoured. Figures 8, 9, 10 and 11 show some of the Mo contour maps for Western Larch and Lodgepole Pine. The corresponding maps for Cu, Zn and Pb are not shown here since, in general, they show extremely poor correlation with the known extent of the deposit due to the exclusion mechanisms operating on these elements. A Cu:Zn ratio map for Larch needles, suggested by many authors as a valuable determinative technique, showed no correlation with the deposit.

Figures 8, 9, 10 and 11 also show the maximum and minimum limits of the deposit as defined by drill hole data (adapted from Kenyon), 1978 plus personal communication). Figure 8 shows the 20 ppm Mo contour for Western Larch needles which conforms, very well, with the deposit outlines. This figure also shows a continuation, or "bulge", of the deposit to the south west along with two previously unknown deposits to the south east and south west. Figure 9 shows the 30 ppm Mo contour for Western Larch first year twigs. It is the next best indicator of the deposit and also shows the "bulge" and new deposits.

| | Overall Range of Mo contents (ppm) | Deposit Range of Mo contents (ppm) | Background Mo (ppm) | Threshold Mo (ppm) |
|---|---|---|---|---|
| LN (needles) | 1.7 - 141.3 | 30 - 70 | 7.5 | 20 |
| L1 (1st year twigs) | 7.2 - 82.7 | 30 - 70 | 12.5 | 30 |
| L2 (2nd year twigs) | 4.0 - 60.3 | 15 - 50 | 9.0 | 10 |
| L3 (3rd year twigs) | trace - 52.5 | 15 - 40 | 8.5 | 10 |
| PN (needles) | 6.8 - 198.7 | 30 - > 100 | 17.5 | 27 |
| P1 (1st year twigs) | 8.1 - 210.9 | 30 - > 100 | 17.5 | 30 |

Table 2. Summary of Western Larch *Larix occidentalis* (L) and Lodgepole Pine *Pinus contorta* (P) Mo content

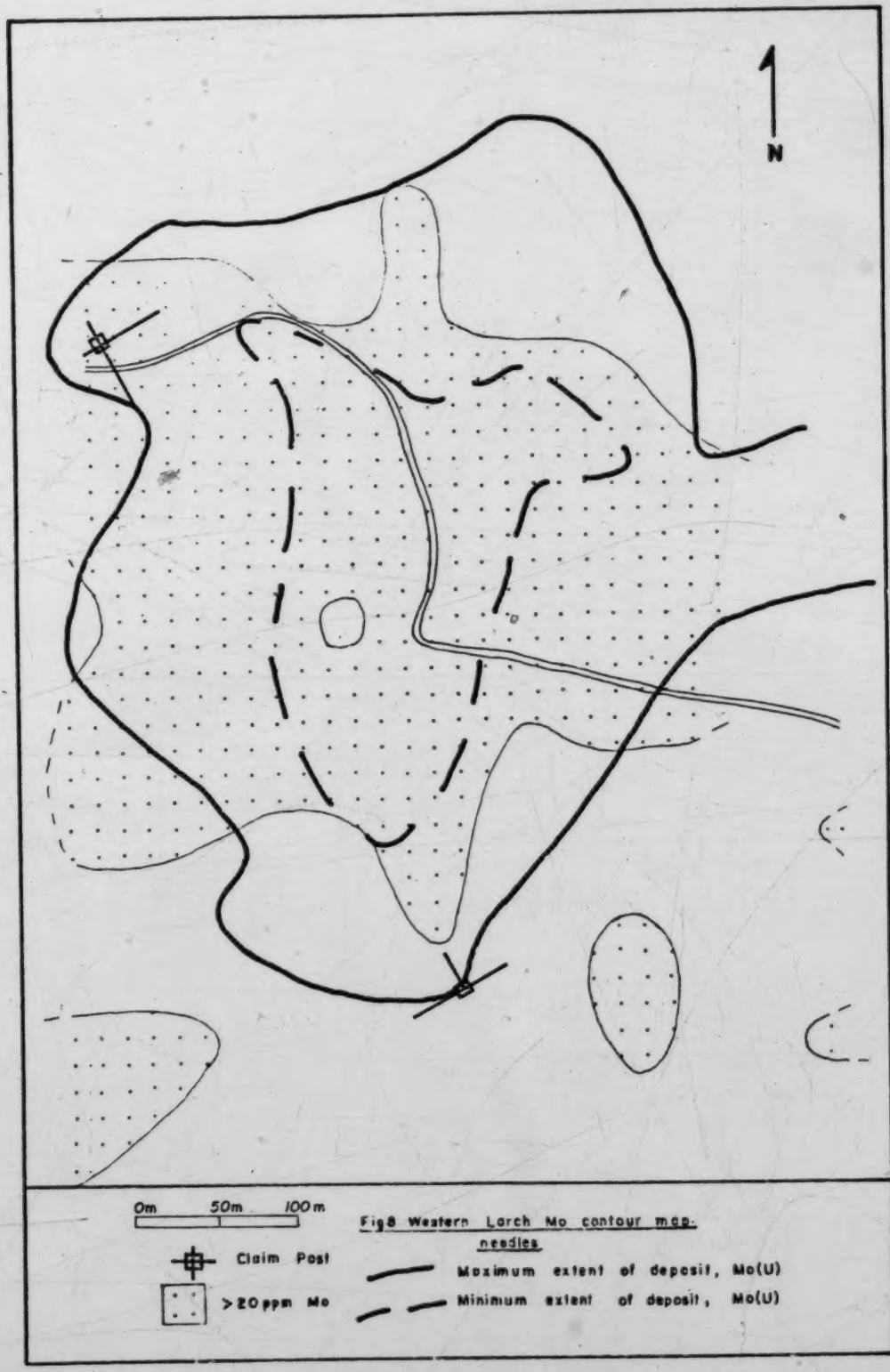


Fig 8 Western Larch Mo contour map: needles

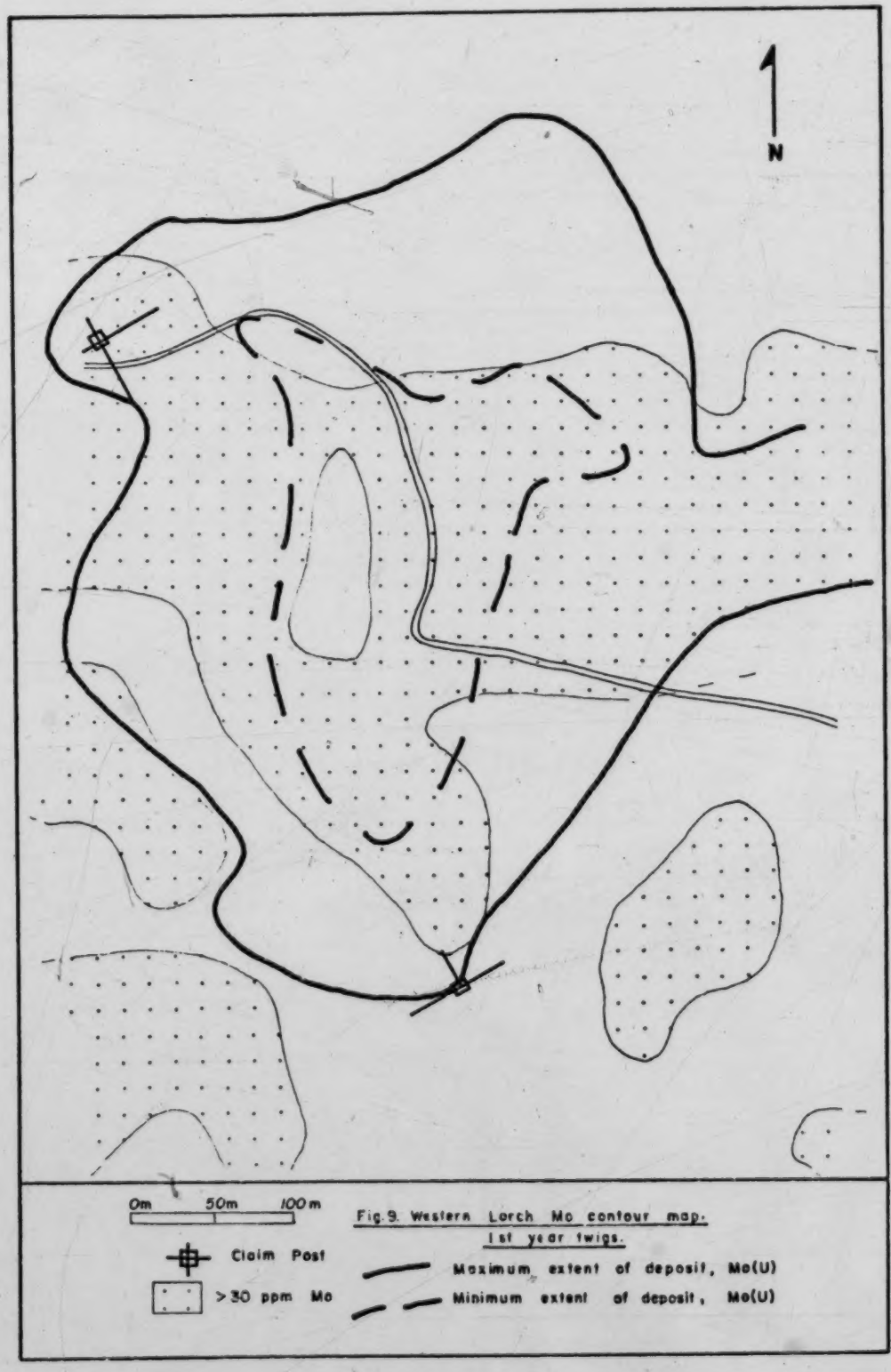


Fig.9. Western Lorch Mo contour map.
1st year twigs.

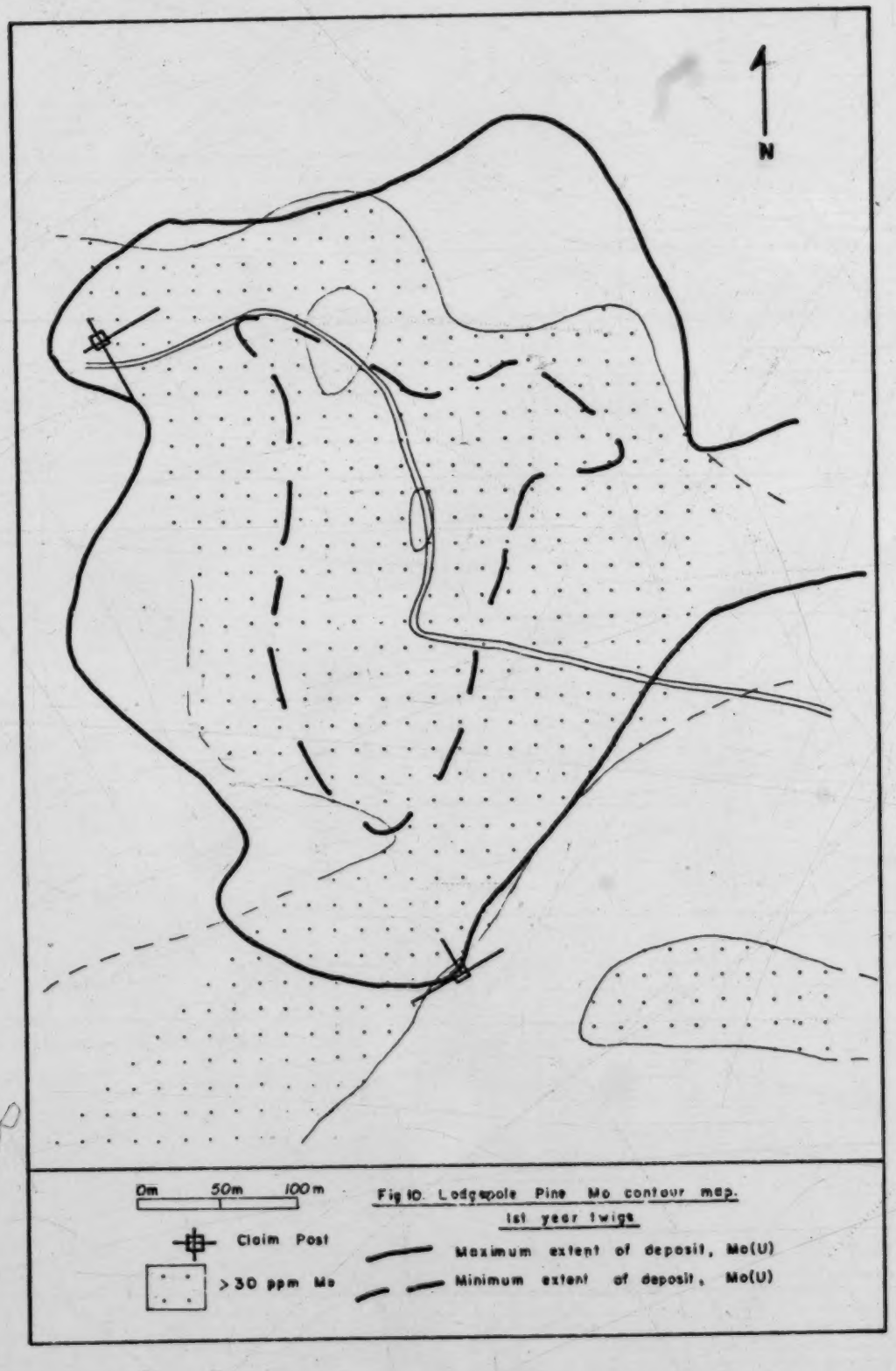


Fig 10. Lodgepole Pine Mo contour map.
1st year twigs

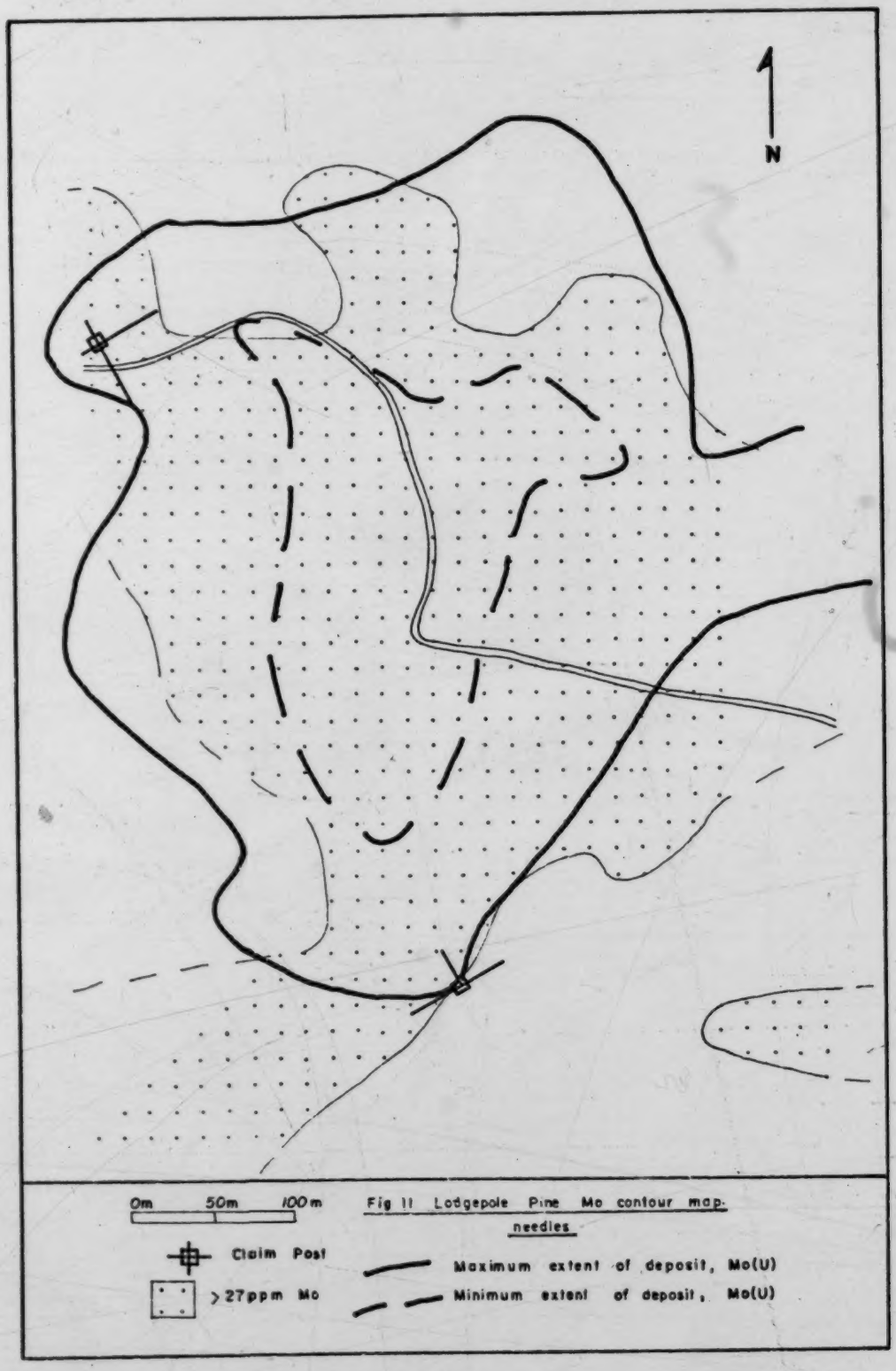


Fig 11 Lodgepole Pine Mo contour map. needles

Figure 10 shows the third best map; 30 ppm Mo contour of Lodgepole Pine twigs. Figure 11, the fourth best fit, shows the 27 ppm Mo contour of Lodgepole Pine needles. These last two maps are not as complete as the Larch maps since Pine trees were absent at many grid points.

Figure 12, the 20 ppm Mo contour for Western Larch second year twigs is included here for two reasons. Firstly, it shows that figures 8, 9, 10 and 11 are not the only ones that define the deposit. They are, however, the best. The second reason is that this figure shows an interesting north-south low "trough" running parallel to and uphill from a logging road. This low was probably caused by a local lowering of the water table, due to the road, which affected either the trees' physiology or the Mo supply to those trees. Therefore, unlike Hornbrook's (1969) Lucky Ship deposit work, this study would suggest that man's disturbance of an area can effect the results of a biogeochemistry survey.

The White Spruce results given at the end of Appendix 5 were compared with Lodgepole Pine values at the same localities in the hope that a relationship could be found between them. This relationship could then be used on White Spruce sampled at sites where Lodgepole Pine was absent in order to bridge the information gap. Unfortunately no relationship existed.

## Soil

Soil data are contained in Appendix 4. This study's Cu and Zn analyses tend to be lower than Vestor's corresponding values. Some of the Mo values are higher, others are lower. This is probably due to

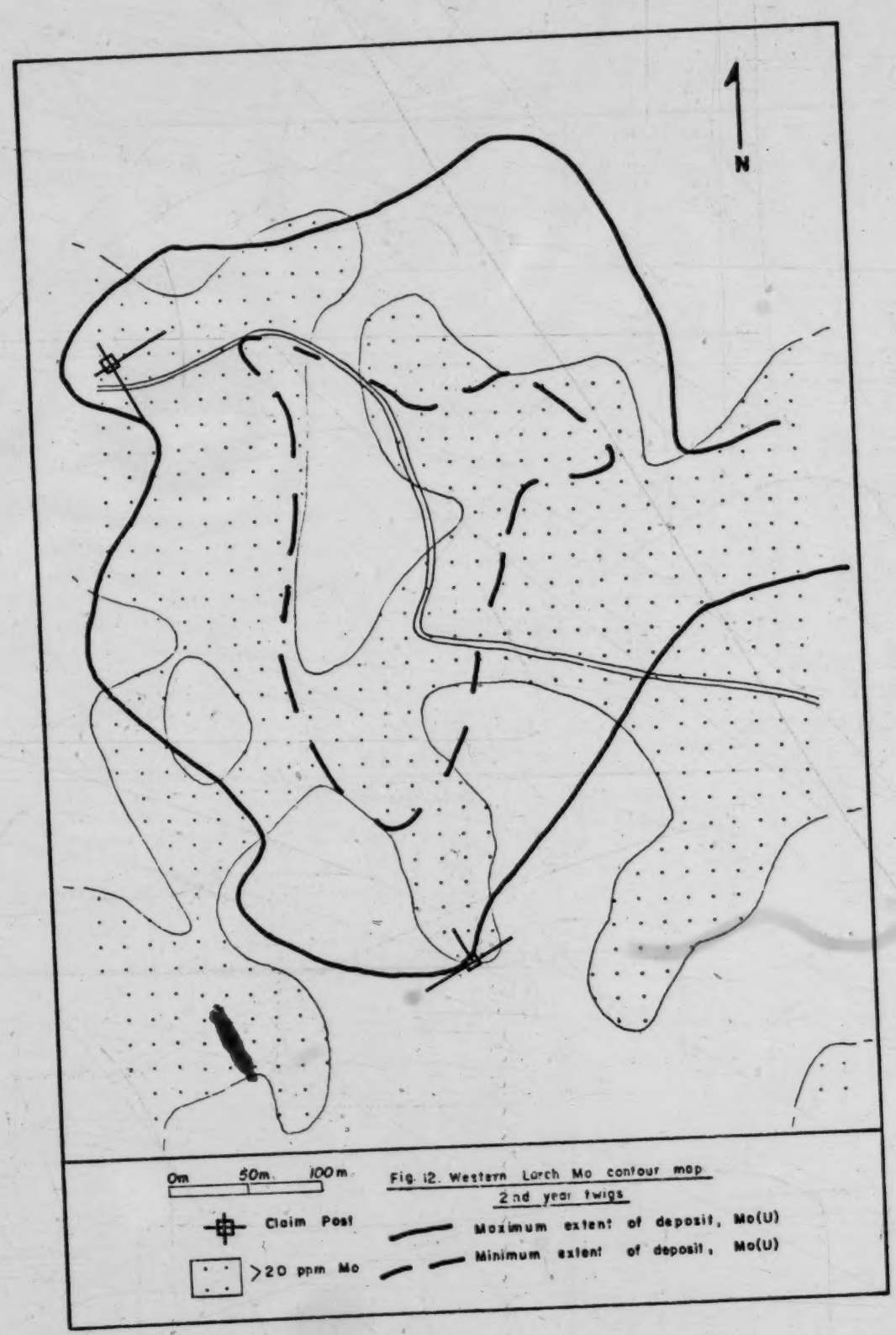


Fig. 12. Western Larch Mo contour map
2nd year twigs

the different horizons sampled by this study and Vestor's.

Background and threshold values were calculated in the same way as vegetation values and are given in table 3. Only the Zn background seems to be higher than might have been expected when compared with table 4. This is probably due to generally higher Zn levels in this region as indicated by the Highland Bell Ag - Pb - Zn mine at Beaverdell.

Figures 13, 14, 15 and 16 show the Mo, Cu, Zn and Pb soil maps. Cu, Zn and Pb do not show the deposit outlines. The 6 ppm Mo threshold contour does show the deposit in broad terms but is not as precise as the various biogeochemical maps in figures 8, 9, 10 and 11. Figure 14 shows an interesting low in the middle of the area which generally corresponds with the deep till depths shown in figure 2. It seems likely that remobilization of Cu had not reached the surface in this area.

## Conclusions

The 20 ppm Mo contour for Western Larch "Larix occidentalis" needles defined the Carmi Mo (U) deposit better than any other vegetation organ or soil medium. It also indicated an extension of the deposit as well as two small, previously unknown, satellite deposits.

The soil Mo anomaly, as published by Kenyon (1978), is much larger than the anomolous vegetation halo. Therefore, soil sampling should be used as a preliminary exploration tool. Once anomalous areas are identified, biogeochemistry, using Western Larch needles should be used to define deposit boundaries.

| | Background (ppm) | Threshold (ppm) |
|---|---|---|
| Mo | 3.0 | 6 |
| Cu | 25.0 | 40 |
| Zn | 125.0 | 200 |
| Pb | 7.5 | 10 |

Table 3. Summary of Soil Mo, Cu, Zn and Pb

Background and Threshold Values at Carmi

| | Average Granodiorite (ppm) | Average Plant Ash (ppm) | Average Soils (ppm) |
|---|---|---|---|
| Mo | 1 | 13 | 25 |
| Cu | 30 | 180 | 20 |
| Zn | 60 | 1400 | 50 |
| Pb | 15 | 70 | 10 |

Table 4. Granodiorite, Plant Ash and Soil Data

These are average values taken from Levinson (1974).

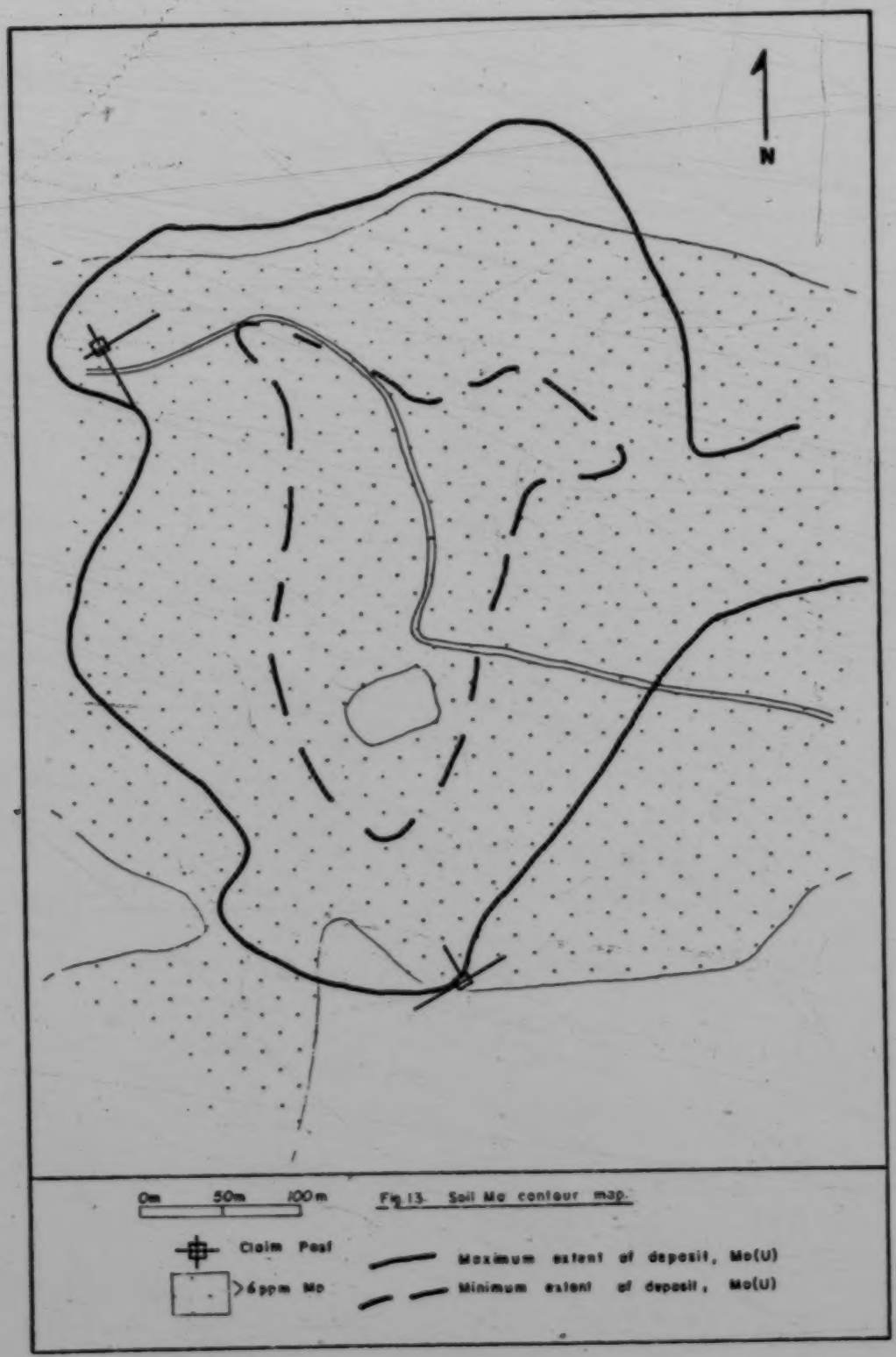


Fig 13. Soil Mo contour map.

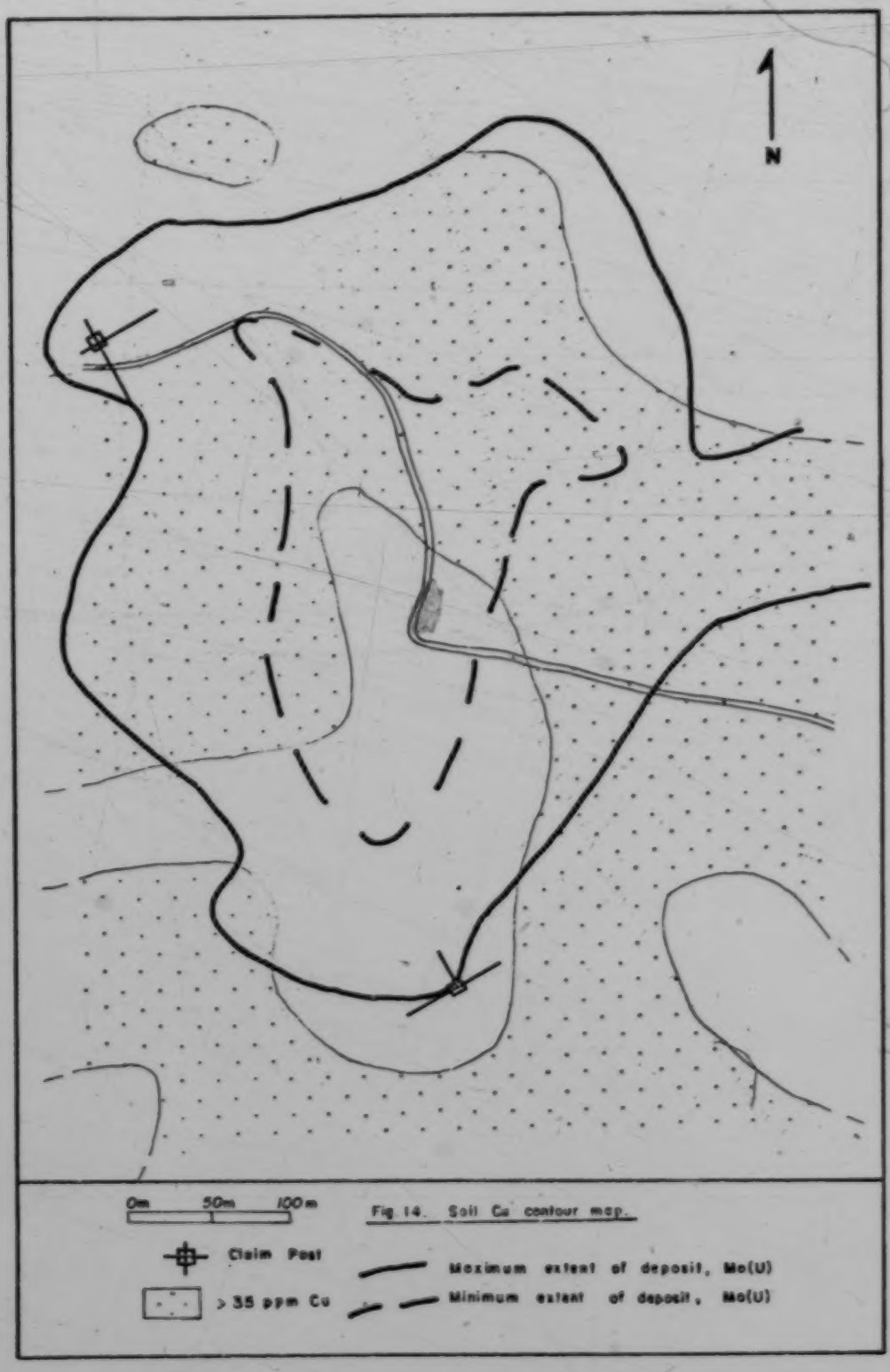


Fig. 14. Soil Cu contour map.

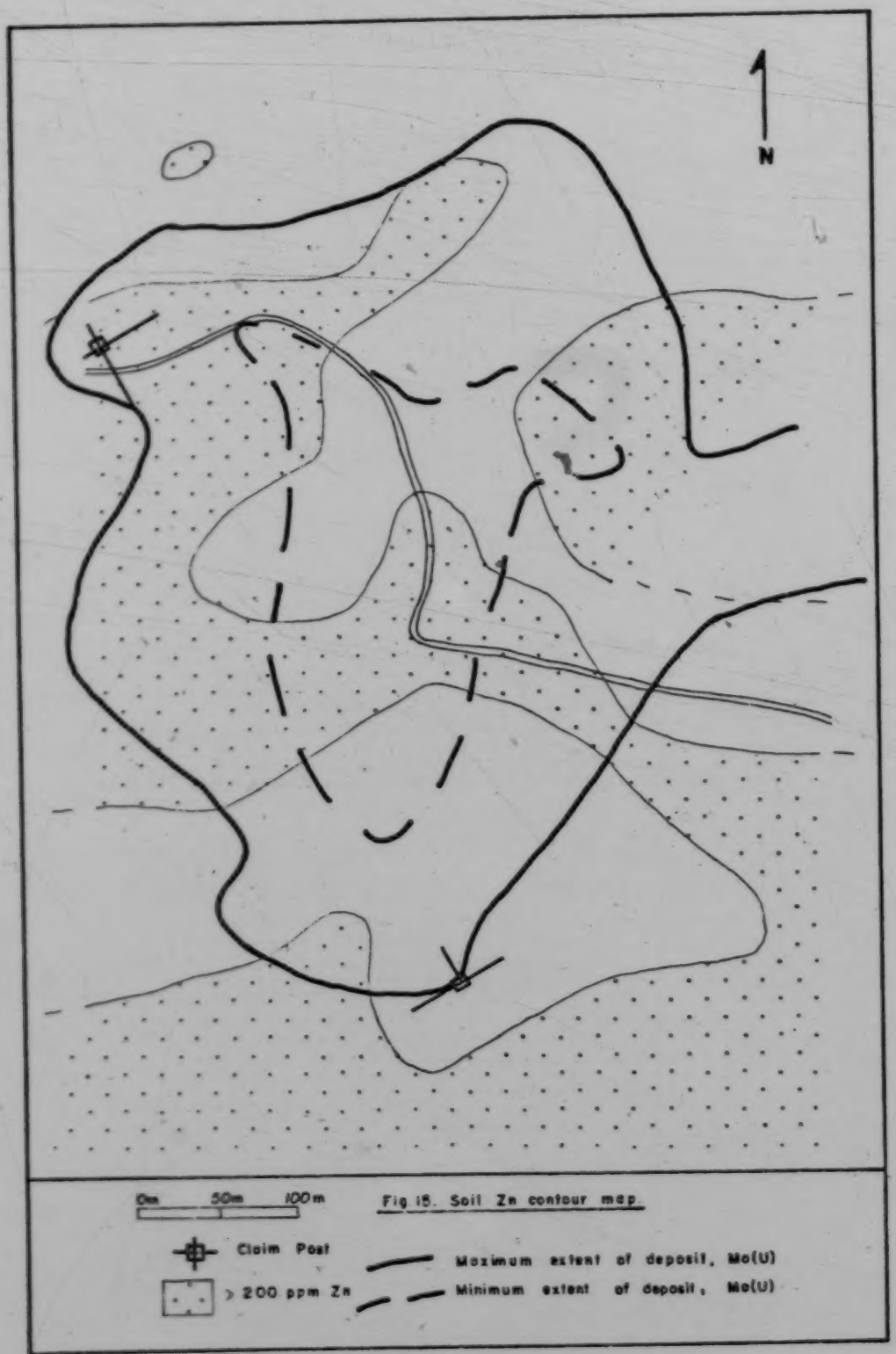


Fig 18. Soil Zn contour map.

Fig 16. Soil Pb contour map.

It should be possible to apply the results of this work to most Nelson Batholith areas with Western Larch growth.

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## APPENDIX I

### LATIN NAMES OF SPECIES MENTIONED

| | |
|---|---|
| Western Larch | *Larix occidentalis* |
| Lodgepole Pine | *Pinus contorta* |
| White Spruce | *Picea glauca* |
| Balsam Fir | *Abies balsamea* |
| Alpine Fir | *Abies Lasiocarpa* |
| Black Spruce | *Picea mariana* |
| Jack Pine | *Pinus banksiana* |
| Sitka Alder | *Alnus sinuata* |
| California Poppy | *Eschscholtzia mexicana* |

## APPENDIX II

## CARMI CLIMATIC MEASUREMENTS

| | J | F | M | A | M | J | J | A | S | O | N | D | Year |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean Rainfall (mm) | 1.3 | 1.8 | 3.3 | 13.5 | 41.1 | 59.2 | 37.3 | 42.7 | 35.3 | 23.6 | 11.4 | 2.0 | 272.5 |
| Mean Snowfall (cm) | 62.2 | 44.2 | 33.5 | 21.8 | 5.8 | 0 | 0 | 0 | 1.0 | 16.3 | 42.2 | 62.2 | 289.2 |
| Mean total precipitation (mm) | 63.8 | 45.7 | 37.3 | 35.3 | 47.2 | 59.2 | 37.3 | 42.7 | 36.1 | 39.9 | 53.8 | 64.3 | 562.6 |
| Mean daily temperature (°C) | -8.1 | -4.3 | -1.9 | 3.3 | 8.3 | 11.6 | 15.5 | 14.7 | 10.8 | 4.8 | -2.4 | -6.2 | 3.8 |
| Number of days with frost | 31 | 28 | 30 | 24 | 10 | 1 | 0 | 0 | 4 | 16 | 28 | 31 | 203 |

This information is based on an average of 25-29 years from 1941-1970.

It comes from Canadian Normals Volumes 2-S1 and 1-S1.

## APPENDIX III

### EXPERIMENTAL SOIL LEACH TECHNIQUE RESULTS

(ppm)

| Sample | Mesh | Leach | Mo | Cu | Zn | Pb |
|---|---|---|---|---|---|---|
| A5 | 40-80 | Hot | 2 | 15 | 105 | 6 |
| | | Cold | 0 | tr | 0 | 0 |
| | <80 | Hot | 2 | 23 | 177 | 8 |
| | | Cold | 0 | tr | 0 | 0 |
| B5 | 40-80 | Hot | 5 | 75 | 151 | 6 |
| | | Cold | 0 | tr | 0 | 0 |
| | <80 | Hot | 7 | 98 | 243 | 8 |
| | | Cold | 0 | tr | 0 | 0 |
| C5 | 40-80 | Hot | 5 | 32 | 73 | 5 |
| | | Cold | 0 | 1.9 | 0 | 0 |
| | <80 | Hot | 9 | 55 | 152 | 8 |
| | | Cold | 0 | 3.4 | 0 | 0 |
| D5 | 40-80 | Hot | 75 | 106 | 7 | 6 |
| | | Cold | 0 | tr | 0 | 0 |
| | <80 | Hot | 72 | 141 | 153 | 10 |
| | | Cold | 0 | tr | 0 | 0 |

| Sample | Mesh | Leach | Mo | Cu | Zn | Pb |
|---|---|---|---|---|---|---|
| E5 | 40-80 | Hot | 20 | 69 | 133 | 6 |
| | | Cold | 0 | tr | 0 | 0 |
| | ∠80 | Hot | 15 | 76 | 249 | 8 |
| | | Cold | 0 | tr | 0 | 0 |
| F5 | 40-80 | Hot | 9 | 23 | 201 | 4 |
| | | Cold | 0 | tr | 0 | 0 |
| | ∠80 | Hot | 9 | 34 | 390 | 6 |
| | | Cold | 0 | tr | 0 | 0 |
| G5 | 40-80 | Hot | 4 | 15 | 58 | 4 |
| | | Cold | 0 | 0.8 | 0 | 0 |
| | ∠80 | Hot | 3 | 21 | 111 | 4 |
| | | Cold | 0 | 0.8 | 0 | 0 |
| H5 | 40-80 | Hot | 97 | 19 | 97 | 5 |
| | | Cold | 0 | 1.0 | 0 | 0 |
| | ∠80 | Hot | 123 | 25 | 148 | 8 |
| | | Cold | 0 | 3.0 | 0 | 0 |
| I5 | 40-80 | Hot | 18 | 19 | 117 | 6 |
| | | Cold | 0 | tr | 0 | 0 |
| | ∠80 | Hot | 13 | 26 | 187 | 8 |
| | | Cold | 0 | tr | 0 | 0 |

| Sample | Mesh | Leach | Mo | Cu | Zn | Pb |
|---|---|---|---|---|---|---|
| J5 | 40-80 | Hot | 3 | 26 | 149 | 9 |
| | | Cold | 0 | tr | 0 | 0 |
| | < 80 | Hot | 2 | 26 | 169 | 9 |
| | | Cold | 0 | 1.0 | 0 | 0 |

## APPENDIX IV

### SOIL ANALYSIS RESULTS (ppm)

(Hot Leach, 80 mesh)

| Sample | Mo | Cu | Zn | Pb |
|---|---|---|---|---|
| A1 | 1 | 30 | 125 | 10 |
| A2 | 2 | 50 | 212 | 11 |
| A3 | 3 | 34 | 172 | 9 |
| A4 | 2 | 25 | 149 | 12 |
| A5 | 1 | 22 | 177 | 8 |
| A6 | 2 | 24 | 123 | 7 |
| A8 | 2 | 19 | 84 | 5 |
| B1 | 2 | 20 | 61 | 7 |
| B4 | 1 | 20 | 108 | 7 |
| B5 | 6 | 97 | 292 | 7 |
| B8 | 9 | 24 | 487 | 10 |
| C1 | 12 | 26 | 259 | 7 |
| C5 | 9 | 55 | 152 | 8 |
| D1 | 33 | 108 | 638 | 11 |
| D5 | 72 | 140 | 152 | 10 |
| E1 | 10 | 20 | 223 | 7 |
| E2 | 30 | 95 | 324 | 9 |
| E3 | 34 | 46 | 8E | 6 |
| E4 | 17 | 37 | 9E | 6 |
| E5 | 15 | 76 | 249 | 8 |

| Sample | Mo | Cu | Zn | Pb |
|---|---|---|---|---|
| E6 | 16 | 57 | 163 | 6 |
| E7 | 19 | 78 | 612 | 8 |
| F1 | 14 | 186 | 360 | 12 |
| F5 | 9 | 34 | 390 | 6 |
| G1 | 13 | 148 | 407 | 9 |
| G5 | 3 | 20 | 111 | 4 |
| H1 | 6 | 18 | 175 | 7 |
| H5 | 123 | 24 | 147 | 7 |
| H9 | 21 | 56 | 275 | 9 |
| I1 | 4 | 54 | 124 | 12 |
| I2 | 5 | 44 | 124 | 7 |
| I3 | 8 | 49 | 128 | 7 |
| I4 | 5 | 18 | 230 | 7 |
| I5 | 13 | 26 | 187 | 8 |
| I6 | 20 | 55 | 137 | 10 |
| I7 | 12 | 47 | 136 | 8 |
| I8 | 13 | 29 | 133 | 9 |
| I9 | 4 | 50 | 325 | 12 |
| J1 | 14 | 83 | 249 | 12 |
| J5 | 1 | 26 | 168 | 8 |
| J9 | 4 | 31 | 212 | 9 |
| K1 | 14 | 19 | 434 | 10 |
| K5 | 4 | 174 | 274 | 10 |
| K9 | 5 | 54 | 205 | 9 |

Error $\pm$ 1 ppm

# APPENDIX V

## VEGETATION ANALYSIS RESULTS

(ppm)

| Sample | Mo | Cu | Zn | Pb |
|---|---|---|---|---|
| A1 LN | 4 | 37 | 801 | 59 |
| 1 | 15 | 229 | 1272 | 71 |
| 2 | 8 | 187 | 2365 | 137 |
| 3 | 7 | 194 | 1871 | 167 |
| PN | 11 | 88 | 3208 | 76 |
| 1 | 13 | 178 | 2862 | 168 |
| A2 LN | 1 | 56 | 415 | 29 |
| 1 | 10 | 209 | 1206 | 294 |
| 2 | 7 | 172 | 1274 | 278 |
| 3 | 4 | 164 | 1319 | 270 |
| PN | 7 | 80 | 2765 | 88 |
| 1 | 8 | 153 | 2075 | 216 |
| A3 LN | 8 | 32 | 384 | 19 |
| 1 | 26 | 207 | 1337 | 180 |
| 2 | 20 | 164 | 1352 | 185 |
| 3 | 18 | 158 | 1390 | 172 |
| PN | 21 | 108 | 3927 | 83 |
| 1 | 29 | 207 | 2166 | 167 |

| Sample | Mo | Cu | Zn | Pb |
|---|---|---|---|---|
| A4 LN | 2 | 31 | 350 | 23 |
| 1 | 8 | 182 | 1167 | 144 |
| 2 | 4 | 142 | 1355 | 185 |
| 3 | 4 | 136 | 1404 | 217 |
| PN | 9 | 104 | 3143 | 86 |
| 1 | 8 | 158 | 2246 | 167 |
| A5 LN | 6 | 36 | 982 | 48 |
| 1 | 7 | 190 | 1388 | 269 |
| 2 | 8 | 191 | 2026 | 290 |
| 3 | 9 | 176 | 2983 | 336 |
| PN | 13 | 98 | 2862 | 73 |
| 1 | 12 | 152 | 1810 | 132 |
| A6 LN | 7 | 37 | 434 | 25 |
| 1 | 9 | 157 | 1234 | 161 |
| 2 | 7 | 140 | 1407 | 208 |
| 3 | 9 | 142 | 1391 | 222 |
| PN | 12 | 94 | 4641 | 90 |
| 1 | 14 | 155 | 2870 | 272 |
| A7 LN | 8 | 42 | 353 | 26 |
| 1 | 10 | 200 | 979 | 230 |
| 2 | 7 | 153 | 1543 | 269 |
| 3 | 8 | 150 | 1919 | 295 |
| PN | 19 | 103 | 2762 | 58 |
| 1 | 22 | 144 | 1971 | 92 |

| Sample | | Mo | Cu | Zn | Pb |
|---|---|---|---|---|---|
| A8 | LN | 5 | 46 | 439 | 46 |
| | 1 | 11 | 172 | 1080 | 285 |
| | 2 | 8 | 148 | 1076 | 302 |
| | 3 | 6 | 160 | 883 | 302 |
| | PN | 8 | 10 | 3280 | 46 |
| | 1 | 10 | 154 | 1976 | 120 |
| A9 | LN | 11 | 38 | 483 | 22 |
| | 1 | 11 | 258 | 1663 | 144 |
| | 2 | 11 | 204 | 2057 | 208 |
| | 3 | 9 | 190 | 2640 | 244 |
| | PN | 32 | 78 | 2744 | 51 |
| | 1 | 25 | 158 | 1676 | 221 |
| B2 | LN | 4 | 43 | 761 | 64 |
| | 1 | 14 | 274 | 1046 | 79 |
| | 2 | 7 | 192 | 2046 | 196 |
| | 3 | 7 | 217 | 2404 | 147 |
| B3 | LN | 11 | 35 | 909 | 40 |
| | 1 | 25 | 189 | 1278 | 250 |
| | 2 | 20 | 126 | 2264 | 263 |
| | 3 | 19 | 147 | 3109. | 311 |
| | PN | 6 | 88 | 3862 | 86 |
| | .1 | 20 | 169 | 2987 | 204 |

| Sample | | Mo | Cu | Zn | Pb |
|---|---|---|---|---|---|
| B4 | LN | 12 | 38 | 1635 | 39 |
| | 1 | 23 | 223 | 1523 | 135 |
| | 2 | 23 | 174 | 2320 | 205 |
| | 3 | 31 | 166 | 3206 | 211 |
| | PN | 67 | 75 | 2531 | 60 |
| | 1 | 45 | 143 | 2192 | 191 |
| B5 | LN | 32 | 34 | 643 | 61 |
| | 1 | 7 | 207 | 1758 | 251 |
| | 2 | 15 | 175 | 2359 | 229 |
| | 3 | 18 | 157 | 2576 | 294 |
| | PN | 30 | 85 | 5058 | 61 |
| | 1 | 27 | 183 | 3160 | 142 |
| B6 | LN | 7 | 38 | 530 | 30 |
| | 1 | 12 | 164 | 1431 | 79 |
| | 2 | 7 | 184 | 2047 | 195 |
| | 3 | 8 | 150 | 2169 | 281 |
| | PN | 9 | 95 | 3037 | 87 |
| | 1 | 16 | 195 | 2011 | 182 |
| B7 | LN | 8 | 45 | 430 | 24 |
| | 1 | 18 | 215 | 1227 | 210 |
| | 2 | 11 | 164 | 1648 | 277 |
| | 3 | 11 | 170 | 1474 | 256 |
| | PN | 16 | 80 | 3212 | 52 |
| | 1 | 13 | 148 | 2439 | 145 |

| Sample | | Mo | Cu | Zn | Pb |
|---|---|---|---|---|---|
| B8 | LN | 16 | 47 | 745 | 29 |
| | 1 | 21 | 186 | 1430 | 161 |
| | 2 | 17 | 173 | 1650 | 215 |
| | 3 | 16 | 164 | 1666 | 274 |
| | PN | 15 | 131 | 2183 | 79 |
| | 1 | 14 | 212 | 1956 | 180 |
| C1 | LN | 62 | 40 | 550 | 122 |
| | 1 | 82 | 275 | 1516 | 192 |
| | 2 | 60 | 209 | 2008 | 221 |
| | 3 | 52 | 198 | 2367 | 248 |
| | PN | 183 | 98 | 5005 | 86 |
| | 1 | 101 | 160 | 2210 | 212 |
| C2 | LN | 38 | 38 | 602 | 25 |
| | 1 | 32 | 205 | 1859 | 86 |
| | 2 | 30 | 160 | 1482 | 195 |
| | 3 | 30 | 178 | 1858 | 265 |
| | PN | 16 | 91 | 2545 | 83 |
| | 1 | 37 | 167 | 1876 | 129 |
| C4 | LN | 7 | 31 | 1061 | 24 |
| | 1 | 11 | 154 | 1663 | 139 |
| | 2 | 18 | 156 | 2563 | 167 |
| | 3 | 15 | 131 | 2510 | 179 |
| | PN | 25 | 105 | 3898 | 75 |
| | 1 | 25 | 149 | 2585 | 125 |

| Sample | | Mo | Cu | Zn | Pb |
|---|---|---|---|---|---|
| C5 | LN | 22 | 25 | 805 | 10 |
| | 1 | 14 | 203 | 1075 | 48 |
| | 2 | 22 | 153 | 1970 | 96 |
| | 3 | 19 | 151 | 2189 | 123 |
| | PN | 30 | 82 | 3515 | 73 |
| | 1 | 34 | 130 | 2786 | 106 |
| C6 | LN | 11 | 27 | 487 | 23 |
| | 1 | 14 | 150 | 1587 | 184 |
| | 2 | 7 | 128 | 1602 | 214 |
| | 3 | 7 | 125 | 1681 | 231 |
| | PN | 18 | 73 | 2655 | 73 |
| | 1 | 19 | 149 | 1676 | 175 |
| C7 | LN | 12 | 46 | 953 | 28 |
| | 1 | 10 | 202 | 1266 | 202 |
| | 2 | 9 | 210 | 2926 | 243 |
| | 3 | 11 | 176 | 2562 | 240 |
| | PN | 49 | 156 | 2877 | 71 |
| | 1 | 49 | 270 | 2599 | 70 |
| C8 | LN | 12 | 33 | 1113 | 33 |
| | 1 | 29 | 245 | 1143 | 112 |
| | 2 | 23 | 180 | 1328 | 126 |
| | 3 | 19 | 162 | 1425 | 197 |
| | PN | 18 | 95 | 2754 | 88 |
| | 1 | 14 | 158 | 1961 | 149 |

| Sample | | Mo | Cu | Zn | Pb |
|---|---|---|---|---|---|
| D2 | LN | 36 | 48 | 520 | 28 |
| | 1 | 45 | 134 | 1001 | 74 |
| | 2 | 34 | 137 | 1378 | 151 |
| | 3 | 27 | 166 | 1503 | 277 |
| | PN | 57 | 61 | 3811 | 72 |
| | 1 | 55 | 137 | 2338 | 187 |
| D3 | LN | 67 | 53 | 481 | 23 |
| | 1 | 37 | 317 | 1183 | 123 |
| | 2 | 32 | 204 | 1348 | 158 |
| | 3 | 30 | 197 | 1375 | 177 |
| D4 | LN | 30 | 33 | 456 | 18 |
| | 1 | 31 | 189 | 1105 | 75 |
| | 2 | 14 | 172 | 1373 | 159 |
| | 3 | 18 | 164 | 1462 | 164 |
| | PN | 28 | 95 | 2972 | 75 |
| | 1 | 30 | 217 | 1811 | 151 |
| D5 | LN | 55 | 43 | 1166 | 50 |
| | 1 | 57 | 238 | 1536 | 180 |
| | 2 | 36 | 199 | 2855 | 1208 |
| | 3 | 41 | 173 | 3449 | 276 |
| | PN | 55 | 94 | 2033 | 97 |
| | 1 | 65 | 200 | 1744 | 404 |

| Sample | | Mo | Cu | Zn | Pb |
|---|---|---|---|---|---|
| D6 | LN | 55 | 28 | 864 | 31 |
| | 1 | 34 | 147 | 1286 | 266 |
| | 2 | 28 | 135 | 1781 | 242 |
| | 3 | 27 | 123 | 2008 | 245 |
| | PN | 122 | 95 | 3179 | 454 |
| | 1 | 210 | 162 | 2161 | 283 |
| D7 | LN | 141 | 47 | 452 | 21 |
| | 1 | 71 | 195 | 1321 | 192 |
| | 2 | 58 | 154 | 1463 | 246 |
| | 3 | 31 | 166 | 1575 | 268 |
| | PN | 198 | 92 | 2459 | 73 |
| | 1 | 187 | 194 | 1989 | 176 |
| D8 | LN | 12 | 41 | 400 | 33 |
| | 1 | 20 | 168 | 1182 | 207 |
| | 2 | 11 | 146 | 1299 | 233 |
| | 3 | 14 | 143 | 1360 | 235 |
| | PN | 6 | 107 | 2548 | 84 |
| | 1 | 9 | 182 | 1777 | 142 |
| D9 | LN | 18 | 32 | 1027 | 41 |
| | 1 | 39 | 192 | 1493 | 202 |
| | 2 | 27 | 168 | 2784 | 237 |
| | 3 | 26 | 153 | 3251 | 270 |
| | PN | 14 | 113 | 2341 | 66 |
| | 1 | 21 | 188 | 2195 | 136 |

| Sample | | Mo | Cu | Zn | Pb |
|---|---|---|---|---|---|
| E1 | LN | 46 | 42 | 1089 | 23 |
| | 1 | 47 | 247 | 1470 | 93 |
| | 2 | 29 | 169 | 1950 | 163 |
| | 3 | 28 | 151 | 2130 | 179 |
| E2 | LN | 48 | 49 | 423 | 33 |
| | 1 | 45 | 265 | 1091 | 142 |
| | 2 | 28 | 228 | 1345 | 174 |
| | 3 | 34 | 192 | 1441 | 194 |
| E3 | LN | 37 | 39 | 430 | 25 |
| | 1 | 46 | 277 | 1107 | 65 |
| | 2 | 28 | 220 | 1409 | 153 |
| | 3 | 21 | 178 | 1573 | 199 |
| E4 | LN | 33 | 38 | 598 | 25 |
| | 1 | 23 | 223 | 1445 | 84 |
| | 2 | 9 | 122 | 1372 | 96 |
| | 3 | 15 | 173 | 2382 | 171 |
| | PN | 77 | 88 | 2922 | 103 |
| | 1 | 69 | 199 | 2341 | 172 |
| E5 | LN | 26 | 41 | 364 | 34 |
| | 1 | 46 | 223 | 1163 | 89 |
| | 2 | 15 | 170 | 1337 | 133 |
| | 3 | 18 | 172 | 1618 | 165 |
| | PN | 31 | 101 | 3318 | 72 |
| | 1 | 26 | 135 | 2051 | 119 |

| Sample | Mo | Cu | Zn | Pb |
|---|---|---|---|---|
| E6 LN | 77 | 44 | 338 | 19 |
| 1 | 43 | 172 | 1188 | 162 |
| 2 | 29 | 160 | 1278 | 196 |
| 3 | 36 | 155 | 1350 | 194 |
| PN | 69 | 109 | 2953 | 58 |
| 1 | 47 | 178 | 2046 | 115 |
| | | | | |
| E7 LN | 33 | 48 | 731 | 51 |
| 1 | 30 | 221 | 1817 | 191 |
| 2 | 26 | 183 | 1777 | 198 |
| 3 | 18 | 154 | 1869 | 149 |
| | | | | |
| F1 LN | 8 | 39 | 725 | 23 |
| 1 | 27 | 204 | 1396 | 65 |
| 2 | 12 | 116 | 1167 | 80 |
| 3 | 21 | 174 | 1913 | 1424 |
| | | | | |
| F2 LN | 35 | 37 | 547 | 47 |
| 1 | 29 | 190 | 1386 | 208 |
| 2 | 21 | 176 | 1703 | 122 |
| 3 | 22 | 183 | 2002 | 154 |
| PN | 29 | 85 | 3392 | 68 |
| 1 | 25 | 196 | 2038 | 142 |
| | | | | |
| F3 LN | 35 | 34 | 490 | 26 |
| 1 | 32 | 160 | 858 | 65 |
| 2 | 22 | 146 | 979 | 109 |
| 3 | 16 | 140 | 1079 | 161 |

| Sample | | Mo | Cu | Zn | Pb |
|---|---|---|---|---|---|
| F4 | LN | 13 | 37 | 564 | 87 |
| | 1 | 15 | 147 | 922 | 73 |
| | 2 | 10 | 145 | 1250 | 120 |
| | 3 | 8 | 147 | 1288 | 130 |
| F5 | LN | 44 | 65 | 475 | 31 |
| | 1 | 71 | 291 | 1544 | 175 |
| | 2 | 43 | 199 | 1673 | 119 |
| | 3 | 47 | 222 | 1990 | 146 |
| G1 | LN | 52 | 40 | 352 | 43 |
| | 1 | 56 | 270 | 957 | 61 |
| | 2 | 36 | 212 | 1149 | 130 |
| | 3 | 29 | 180 | 1221 | 171 |
| G2 | LN | 28 | 41 | 457 | 36 |
| | 1 | 27 | 192 | 915 | 73 |
| | 2 | 6 | 184 | 1402 | 137 |
| | 3 | 6 | 175 | 1689 | 164 |
| G3 | LN | 45 | 29 | 615 | 62 |
| | 1 | 31 | 164 | 1336 | 439 |
| | 2 | 24 | 153 | 1778 | 153 |
| | 3 | 18 | 141 | 1674 | 188 |
| | PN | 75 | 91 | 2496 | 78 |
| | 1 | 54 | 190 | 2110 | 212 |

| Sample | | Mo | Cu | Zn | Pb |
|---|---|---|---|---|---|
| G4 | LN | 72 | 54 | 876 | 29 |
| | 1 | 69 | 199 | 1284 | 74 |
| | 2 | 49 | 161 | 1646 | 90 |
| | 3 | 44 | 142 | 1806 | 114 |
| G5 | LN | 25 | 49 | 869 | 39 |
| | 1 | 29 | 155 | 1109 | 132 |
| | 2 | 17 | 211 | 2404 | 120 |
| | 3 | 14 | 166 | 2390 | 139 |
| G6 | LN | 15 | 29 | 532 | 22 |
| | 1 | 15 | 191 | 1601 | 167 |
| | 2 | 16 | 151 | 2046 | 219 |
| | 3 | 14 | 138 | 1966 | 213 |
| G7 | LN | 33 | 35 | 463 | 30 |
| | 1 | 29 | 154 | 1592 | 250 |
| | 2 | 20 | 134 | 1737 | 248 |
| | 3 | 24 | 132 | 1949 | 262 |
| | PN | 54 | 117 | 3620 | 58 |
| | 1 | 32 | 206 | 3152 | 92 |
| H1 | LN | 24 | 33 | 763 | 25 |
| | 1 | 29 | 136 | 1592 | 107 |
| | 2 | 16 | 129 | 2016 | 177 |
| | 3 | 18 | 129 | 1936 | 189 |

| Sample | | Mo | Cu | Zn | Pb |
|---|---|---|---|---|---|
| H2 | LN | 31 | 42 | 369 | 36 |
| | 1 | 45 | 281 | 1136 | 74 |
| | 2 | 31 | 227 | 1247 | 110 |
| | 3 | 18 | 222 | 1431 | 159 |
| H3 | LN | 15 | 37 | 380 | 16 |
| | 1 | 29 | 336 | 1542 | 130 |
| | 2 | 20 | 242 | 1711 | 154 |
| | 3 | 18 | 200 | 1669 | 156 |
| H4 | LN | 17 | 26 | 660 | 17 |
| | 1 | 30 | 208 | 1341 | 65 |
| | 2 | 17 | 161 | 1731 | 124 |
| | 3 | 9 | 149 | 2063 | 149 |
| | PN | 28 | 89 | 4955 | 67 |
| | 1 | 19 | 183 | 4443 | 114 |
| H5 | LN | 21 | 39 | 651 | 17 |
| | 1 | 42 | 225 | 1246 | 73 |
| | 2 | 29 | 173 | 1601 | 117 |
| | 3 | 26 | 155 | 1734 | 148 |
| | PN | 37 | 87 | 7433 | 64 |
| | 1 | 37 | 217 | 5162 | 123 |
| H6 | LN | 6 | 33 | 1502 | 20 |
| | 1 | 13 | 136 | 1283 | 100 |
| | 2 | 9 | 127 | 1511 | 168 |
| | 3 | 9 | 124 | 1626 | 180 |

| Sample | Mo | Cu | Zn | Pb |
|---|---|---|---|---|
| H7 LN | 6 | 37 | 517 | 17 |
| 1 | 24 | 212 | 1036 | 82 |
| 2 | 17 | 179 | 1200 | 161 |
| 3 | 9 | 168 | 1388 | 166 |
| PN | 30 | 193 | 713 | 216 |
| 1 | 27 | 97 | 2471 | 85 |
| H8 LN | 9 | 24 | 564 | 22 |
| 1 | 43 | 193 | 1196 | 102 |
| 2 | 22 | 108 | 1402 | 142 |
| 3 | 25 | 141 | 1794 | 210 |
| PN | 23 | 86 | 3377 | 83 |
| 1 | 15 | 150 | 1966 | 133 |
| H9 LN | 20 | 36 | 485 | 27 |
| 1 | 23 | 155 | 928 | 101 |
| 2 | 21 | 158 | 1411 | 162 |
| 3 | 16 | 159 | 1576 | 225 |
| PN | 12 | 97 | 4548 | 87 |
| 1 | 14 | 207 | 4107 | 143 |
| I2 LN | 18 | 46 | 412 | 21 |
| 1 | 29 | 218 | 1239 | 109 |
| 2 | 20 | 196 | 1703 | 176 |
| 3 | 21 | 190 | 1730 | 181 |

| Sample | Mo | Cu | Zn | Pb |
|---|---|---|---|---|
| I4 LN | 7 | 23 | 788 | 22 |
| 1 | 9 | 139 | 1621 | 142 |
| 2 | 4 | 140 | 2033 | 171 |
| 3 | trace | 137 | 2257 | 199 |
| PN | 27 | 92 | 2842 | 59 |
| 1 | 36 | 155 | 1700 | 108 |
| I5 LN | 20 | 26 | 334 | 13 |
| 1 | 32 | 131 | 819 | 147 |
| 2 | 24 | 122 | 1071 | 195 |
| 3 | 18 | 128 | 1249 | 231 |
| PN | 37 | 75 | 2500 | 106 |
| 1 | 42 | 156 | 1659 | 175 |
| I6 LN | 11 | 37 | 423 | 15 |
| 1 | 17 | 258 | 1078 | 80 |
| 2 | 11 | 180 | 1369 | 136 |
| 3 | 9 | 171 | 1489 | 169 |
| PN | 17 | 55 | 2613 | 80 |
| 1 | 18 | 134 | 1909 | 169 |
| I7 LN | 21 | 32 | 410 | 18 |
| 1 | 47 | 221 | 1362 | 138 |
| 2 | 22 | 177 | 1501 | 206 |
| 3 | 20 | 188 | 1632 | 241 |
| PN | 24 | 89 | 2694 | 98 |
| 1 | 25 | 156 | 1569 | 200 |

| Sample | Mo | Cu | Zn | Pb |
|---|---|---|---|---|
| I8 LN | 19 | 24 | 403 | 16 |
| 1 | 49 | 136 | 947 | 53 |
| 2 | 34 | 141 | 1306 | 99 |
| 3 | 20 | 125 | 1485 | 141 |
| PN | 24 | 105 | 3177 | 57 |
| 1 | 22 | 130 | 1740 | 113 |
| | | | | |
| I9 LN | 6 | 44 | 518 | 31 |
| 1 | 7 | 183 | 1026 | 169 |
| 2 | 7 | 137 | 1020 | 207 |
| 3 | 6 | 155 | 1222 | 217 |
| PN | 20 | 91 | 2464 | 88 |
| 1 | 13 | 190 | 1783 | 146 |
| | | | | |
| J1 LN | 65 | 39 | 379 | 34 |
| 1 | 33 | 117 | 834 | 80 |
| 2 | 46 | 212 | 1358 | 175 |
| 3 | 34 | 204 | 1580 | 204 |
| | | | | |
| J2 LN | 95 | 35 | 421 | 48 |
| 1 | 65 | 154 | 1051 | 112 |
| 2 | 58 | 151 | 1314 | 146 |
| 3 | 49 | 142 | 1599 | 172 |
| PN | 54 | 131 | 3988 | 87 |
| 1 | 77 | 172 | 2253 | 112 |

| Sample | Mo | Cu | Zn | Pb |
|---|---|---|---|---|
| J3 LN | 19 | 40 | 364 | 37 |
| 1 | 31 | 136 | 881 | 41 |
| 2 | 29 | 146 | 1103 | 109 |
| 3 | 22 | 157 | 1267 | 146 |
| J4 LN | 11 | 31 | 369 | 31 |
| 1 | 21 | 150 | 1181 | 167 |
| 2 | 12 | 117 | 1271 | 184 |
| 3 | 10 | 119 | 1279 | 177 |
| PN | 49 | 133 | 3635 | 71 |
| 1 | 53 | 245 | 3085 | 208 |
| J5 LN | 8 | 24 | 388 | 38 |
| 1 | 19 | 216 | 1126 | 78 |
| 2 | 17 | 177 | 1297 | 147 |
| 3 | 6 | 224 | 1193 | -- |
| PN | 23 | 94 | 2299 | 86 |
| 1 | 19 | 172 | 1821 | 167 |
| J6 LN | 4 | 59 | 421 | 54 |
| 1 | 20 | 203 | 1242 | 162 |
| 2 | 16 | 195 | 1595 | 231 |
| 3 | 10 | 167 | 1897 | 298 |
| PN | 16 | 104 | 2714 | 68 |
| 1 | 17 | 200 | 2206 | 174 |

| Sample | | Mo | Cu | Zn | Pb |
|---|---|---|---|---|---|
| J7 | LN | 24 | 28 | 428 | 31 |
| | 1 | 33 | 135 | 967 | 83 |
| | 2 | 22 | 123 | 1113 | 119 |
| | 3 | 19 | 116 | 1209 | 128 |
| | PN | 16 | 114 | 3036 | 81 |
| | 1 | 38 | 270 | 1679 | 136 |
| J8 | LN | 7 | 32 | 297 | 32 |
| | 1 | 20 | 160 | 1064 | 172 |
| | 2 | 9 | 280 | 1287 | 246 |
| | 3 | 10 | 132 | 1324 | 221 |
| | PN | 28 | 98 | 2392 | 62 |
| | 1 | 35 | 202 | 2390 | 125 |
| J9 | LN | 27 | 16 | 300 | 30 |
| | 1 | 22 | 170 | 1128 | 120 |
| | 2 | 13 | 172 | 1295 | 163 |
| | 3 | 12 | 134 | 1401 | 199 |
| | PN | 44 | 81 | 2382 | 69 |
| | 1 | 37 | 124 | 1790 | 122 |
| K1 | LN | 46 | 37 | 468 | 39 |
| | 1 | 46 | 228 | 1426 | 105 |
| | 2 | 32 | 153 | 1684 | 134 |
| | 3 | 31 | 166 | 1777 | 152 |
| | PN | 108 | 90 | 4367 | 61 |
| | 1 | 89 | 217 | 3284 | 99 |

| Sample | Mo | Cu | Zn | Pb |
|---|---|---|---|---|
| K2 LN | 15 | 46 | 489 | 25 |
| 1 | 20 | 230 | 1244 | 104 |
| 2 | 10 | 142 | 1322 | 113 |
| 3 | 7 | 187 | 1679 | 180 |
| PN | 36 | 118 | 3746 | 63 |
| 1 | 68 | 337 | 2625 | 127 |
| | | | | |
| K3 LN | 16 | 35 | 552 | 36 |
| 1 | 47 | 157 | 1095 | 87 |
| 2 | 20 | 153 | 1490 | 123 |
| 3 | 26 | 150 | 1619 | 163 |
| | | | | |
| K4 LN | 4 | 25 | 395 | 21 |
| 1 | 13 | 152 | 929 | 107 |
| 2 | 9 | 117 | 1130 | 147 |
| 3 | 5 | 128 | 1277 | 170 |
| PN | 19 | 169 | 2542 | 57 |
| 1 | 23 | 82 | 1895 | 140 |
| | | | | |
| K5 LN | 6 | 36 | 567 | 41 |
| 1 | 14 | 164 | 1277 | 213 |
| 2 | 11 | 125 | 1444 | 208 |
| 3 | 9 | 141 | 1569 | 232 |
| PN | 10 | 122 | 3253 | 78 |
| 1 | 15 | 186 | 2038 | 85 |

| Sample | Mo | Cu | Zn | Pb |
|---|---|---|---|---|
| K6 LN | 11 | 34 | 456 | 33 |
| 1 | 18 | 165 | 1178 | 141 |
| 2 | 8 | 149 | 1515 | 202 |
| 3 | 13 | 149 | 1806 | 216 |
| | | | | |
| K7 LN | 13 | 33 | 277 | 37 |
| 1 | 27 | 122 | 836 | 94 |
| 2 | 15 | 122 | 944 | 142 |
| 3 | 13 | 122 | 1120 | 185 |
| PN | 10 | 131 | 2598 | 84 |
| 1 | 10 | 196 | 2010 | 150 |
| | | | | |
| K8 LN | 6 | 24 | 470 | 27 |
| 1 | 11 | 222 | 1073 | 59 |
| 2 | 5 | 151 | 1228 | 94 |
| 3 | 3 | 140 | 1331 | 131 |
| PN | 8 | 90 | 2763 | 79 |
| 1 | 15 | 176 | 3245 | 213 |
| | | | | |
| K9 LN | 18 | 29 | 362 | 48 |
| 1 | 38 | 143 | 1092 | 123 |
| 2 | 26 | 124 | 1229 | 164 |
| 3 | 22 | 126 | 1290 | 173 |

Error for Mo, Cu and Pb is $\pm$ 1.5 ppm

Error for Zn is $\pm$ 40 ppm